THE

LONDON, EDINBURGH, AND DUBLIN

PHILOSOPHICAL MAGAZINE

AND

JOURNAL OF SCIENCE.

CONDUCTED BY

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AND

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"Nec aranearum sane textus ideo melior quia ex se fila gignunt, nec noster vilior quia ex alienis libamus ut apes." JUST. LIPS. *Polit.* lib. i. cap. 1. Not.

VOL. IV.—FIFTH SERIES.

JULY—DECEMBER 1877.

LONDON.

TAYLOR AND FRANCIS, RED LION COURT, FLEET STREET,

Printers and Publishers to the University of London;

SOLD BY LONGMANS, GREEN, READER, AND DYER; KENT AND CO.; SIMPKIN, MARSHALL, AND CO.; AND WHITTAKER AND CO.;—AND BY ADAM AND CHARLES BLACK, AND THOMAS CLARK, EDINBURGH; SMITH AND SON, GLASGOW:—HODGES, FOSTER, AND CO, DUBLIN:—PUTNAM, NEW YORK:—AND ASHER AND CO., BERLIN.

"Meditationis est perscrutari occulta; contemplationis est admirari perspicua . . . . . Admiratio generat quæstionem, quæstio investigationem, investigatio inventionem."—*Hugo de S. Victore.*

—"Cur spirent venti, cur terra dehiscat,
Cur mare turgescat, pelago cur tantus amaror,
Cur caput obscura Phœbus ferrugine condat,
Quid toties diros cogat flagrare cometas;
Quid pariat nubes, veniant cur fulmina cœlo,
Quo micet igne Iris, superos quis conciat orbes
Tam vario motu."

J. B. Pinelli ad Mazonium.

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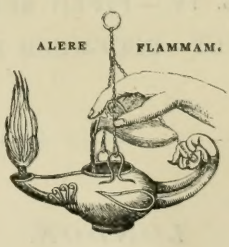

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[FIFTH SERIES.]

JULY 1877.

I. *On Fallible Measures of Variable Quantities, and on the Treatment of Meteorological Observations.* By G. H. DARWIN, *M.A., Fellow of Trinity College, Cambridge**.

IF we make any observation, for example the transit of a star, a definite numerical result is obtained. To say that that result is liable to errors of observation, is only correct from one point of view. It is true that the result does not really correspond with the time at which the star crossed the meridian, yet it *is* an accurate representation of a certain very complex event. Undoubtedly, the principal feature in that event is the time of crossing the meridian; but there is also involved in it various properties of the instruments, the atmosphere, and the observer himself, &c. The object of the observation is, of course, to get a result which shall represent that principal feature, after the elimination of the minor features. The comparative simplicity of this, and of many other observations, permits us to unravel the complex event into its constituent parts, and to estimate each numerically. One part consists of corrections of all sorts. But when all these have been made, there still remains a result representing a complex event, viz. the transit of the star, together with unknown properties of the circumstances of the observation. These unknown properties form the subject-matter of the theory of errors of observation; but it is only because there is a consistent theory of the principal phenomenon, that the most probable line of demarcation can be drawn between the two parts of the complex event. The final result is given as a definite value with a margin of uncertainty in either direction.

But in the case of astronomical observations there is com-

* Communicated by the Author.

plete certainty that we cannot have affected the principal event in any way by the method of observing. In experiments, however, it is impossible to imitate exactly the proposed conditions ; so that, even when corrections have been applied, and when we can estimate the degree of uncertainty in the method of observing, there remains another sort of uncertainty, viz. as to the closeness with which the proposed conditions were imitated ; that is to say, the principal event is rendered uncertain and complex.

The case of experiments graduates into that of observations of natural phenomena, where we have no control over the disturbing causes, and have no opportunity of slightly altering the conditions.

The line of demarcation between the principal event, whose laws are to be determined, and the disturbances, here becomes still more undefined. And where we are still groping after a law of the phenomena (as in the case of meteorology) it is unknown what is to be classed as the principal event and what as disturbances. It is like looking at a series of irregular waves with ripples of various sizes on their surface ; until some law in the formation of the waves is discovered, it is unknown how large a ripple may be neglected in the discovery of that law. Nevertheless the only chance of discovery seems to be to neglect the ripples by some arbitrary rule, and to examine the main features of the series of waves.

The problem of how best to combine a number of discontinuous observations into a continuous law, so as to give a general representation of them after disturbances due to fallibility of measures, runs of chance (as in statistics), &c. have been set aside, is one that constantly presents itself for solution ; and a rational and methodical treatment can hardly fail to be of value.

The most frequent occasion for the solution of the problem arises from the necessity of drawing a curve passing close to the extremities of a number of ordinates ; and the usual way of solving it is to draw a curve without abrupt changes of curvature as close to the points as possible. If the changes of curvature are abrupt enough, the curve may be made to pass exactly through the points ; but then each observation is treated as exact, and we have exactly the case of the series of waves with ripples on them. But, by what precedes, it appears that we had better omit the ripples ; and the question remains as to how far we are justified in smoothing down the curve. This process of smoothing is often done by the free hand ; but it will probably be done better by a system ; and it will be an additional advantage if the system admits of arithmetical as well as graphical application.

In those cases in which an algebraic law can be assigned, to which the ordinates ought to conform, the best method of treating the problem is to determine the constants involved in the function by the method of least squares; but it might often be not worth while to carry out this process, as, for example, where the deviations of the various observations from the law are large, and where it would accordingly be pedantic to assign values to the constants with precision.

Where the law is unknown and the observations are equidistant, a method of treatment might, perhaps, be devised by the assumption of some form of function containing fewer constants than the number of given points, and consisting of a number of simple harmonic terms, none of which go through a large fraction of their period in passing from one ordinate to the next. The constants involved might then be determined by the method of least squares, so that the function should give the best representation of the observations. But the assumption of the form of function would be arbitrary, and the process very laborious.

On the whole it will be more convenient and equally satisfactory, as far the result is concerned, to proceed empirically from the first, remembering that the main object is to exclude ripples of short period.

The method here suggested is one which I believe is used in some form or other by meteorologists; but I am not aware that its merits have been discussed, or that it has been extended to the smoothing of surfaces and of functions of three or more independent variables, as I here propose to do*.

Empirical Rule.—The observations are supposed to be equidistant and to be functions of only one independent variable. The method may be most easily explained geometrically, and the transition afterwards made to its arithmetical equivalent. It will be convenient also to speak of the deviations of the several observations from the principal part of the complex event which those observations represent as *errors*.

It is proposed to substitute for each pair of consecutive points A, B, a point P which bisects the straight line A B. The points P then lie on a series of ordinates halfway between the original ones.

If the errors of A and B are of opposite sign, P is a better point than either of them; if they have errors of the

* Since this paper has been in the hands of the printer, I have learnt that M. Schiapparelli has written a work entitled *Sul modo di ricavare la vera expressione delle leggi della natura dalle curve empiriche*; (Milan, 1867), and that M. De Forest has written on the subject in the 'Annual Reports of the Smithsonian Institution' for 1871 and 1873, and in the 'Analyst (Iowa) for May 1877.

same sign, P will be better or worse according to the direction of the curvature of the curve. But if the rate of change of curvature of the curve is small (as it must be assumed to be to justify the smoothing process), P is very little better or worse. Now, as on the average the series of points deviate as often to one side as to the other of the curve, there clearly will be on the average an improvement in accuracy from the substitution of P, whilst there will certainly be less abrupt changes of curvature in a curve passing through P than through A B. Where the points already lie on a fair curve with no contrary flexure, the chance is rather more than even that there will be a loss of accuracy of representation, because the substituted points all lie on the same side of the given ones, and the only case where there is improvement is where all the errors have one particular sign, and are not very small. The process of smoothing must then be applied cautiously, and especially at maximum- and minimum-points.

If the points P do not lie on a fair curve, the process may be applied again in part of the series or along the whole line; but when once our judgment leads us to think that the curve is smooth enough, every succeeding operation tends to spoil the representation.

Analytically the process may be stated as follows:—

If y_0, y_1, y_2, &c. be the successive given ordinates, and if ϕ indicates a single smoothing operation, so that ϕy_x indicates the substituted ordinate corresponding to the abscissa x; then clearly

$$\phi y_x = \tfrac{1}{2}(y_{x+\frac{1}{2}} + y_{x-\frac{1}{2}}),$$

and generally

$$\phi^n y_x = \left(\frac{\mathrm{E}^{\frac{1}{2}} + \mathrm{E}^{-\frac{1}{2}}}{2}\right)^n y_x.$$

It is clear that an odd number of operations will leave us with points on ordinates halfway between the original ones, whilst an even number will leave us on the original ones. There is a practical advantage in proceeding by two operations at a time, because it is not then necessary to draw the intermediate ordinates, and because a double operation has a very simple geometrical and analytical meaning.

From the above formula,

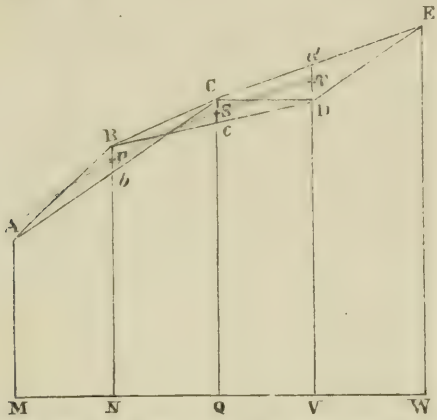
$$\phi^2 y_x = \tfrac{1}{2}\left\{ y_x + \frac{y_{x+1} + y_{x-1}}{2} \right\}.$$

If in the figure M A, N B, Q C are the three ordinates y_{x-1}, y_x, y_{x+1}, then $Nb = \frac{1}{2}(y_{x+1} + y_{x-1})$, and P, which bisects B$b$, is the point to be substituted for B.

The practical rule of construction may be stated thus:—

Let A, B, C, &c. be the given points; join every point to

that next it and next but one to it. Then the points to be substituted bisect the intercepts B b, C c, &c. in P, S &c. If the curve which may be drawn through P, S &c. still seems too sinuous, repeat the operation.



The arithmetical application of this process is obviously very simple; for

$$\phi^2 y_x = y_x + \tfrac{1}{4}\{y_{x-1} - 2y_x + y_{x+1}\}$$
$$= y_x + \tfrac{1}{4}\Delta^2 y_{x-1};$$

and therefore the correction to be applied to any ordinate y_x is is $\frac{1}{4}\Delta^2 y_{x-1}$.

We can see how it is that this process tends to improve the curve. The observed or given values of the function consist of two parts, the first representing the principal event or wave whose law of variation is to be found, and the second the errors or ripples which are to be eliminated. Now the observations are supposed to be so close as not to admit of very large differences between the successive values of the *principal event*; and therefore their second differences will be small. On the other hand, the errors will be some positive and some negative; and therefore their second differences will be very irregular, and probably much larger on the whole than the errors themselves. The second differences of the observed values are the sums formed by the addition of these two sets of second differences; and the justifiability of the process depends on the assumption that the increase of the latter will be sufficient to render the diminished values of the former insignificant by comparison. We thus obtain a series of quantities which depend principally on the errors, except in case the errors are small, or in case of a run of luck in the signs and magnitude of the errors, such as to make them apparently conform to law

and thus present small second differences. Now the proposed corrections to the various observed values are the quarters of this series of quantities; and thus in all probability our corrections depend principally on the errors. The process is therefore justifiable unless the points already lie in a smooth curve. The rough criterion of the applicability of the smoothing process is that the second differences of the observed values should not appear to conform to any law.

Every double operation causes the loss of one point at the beginning and one at the end; but perhaps the best course is to treat the first and last points as exact; and if the operation is repeated more than twice, the second and last but one as exact after one of these double operations, and so on.

Polar Coordinates.—The preceding method is applicable with equal justice to the case of polar coordinates, where the ordinates are replaced by radii vectores.

Irregular Observations.—With observations which are not equidistant, a strictly analogous process would be complex; but as it is empirical, a slight modification will be permissible. Thus we may omit the analogue of interpolation on intermediate ordinates, and only retain the double operation. The intercepts B b, C c, &c. may be bisected as before; for this gives less weight to observations which are more remote than to those which are near, as it clearly ought to do.

The corresponding numerical rule is to substitute for the ordinate y_r, the value

$$\frac{(x_{r+1}-x_r)(y_{r-1}+y_r)+(x_r-x_{r-1})(y_r+y_{r+1})}{2(x_{r+1}-x_{r-1})},$$

where

$$x_{r-1},\ y_{r-1};\ x_r,\ y_r;\ x_{r+1},\ y_{r+1}$$

are the coordinates of the three successive points.

The merits of an empirical rule like this must of course depend on how it seems to work practically. I therefore devised the following scheme for testing it. A circular piece of card was graduated radially, so that a graduation marked x was $\frac{720}{\sqrt{\pi}}\int_0^x e^{-x^2}dx$ degrees distant from a fixed radius. The card was made to spin round its centre close to a fixed index. It was then spun a number of times, and on stopping it the number opposite the index was read off*. From the nature of the graduation the numbers thus obtained will occur in exactly the same way as errors of observation occur in practice; but

* It is better to stop the disk when it is spinning so fast that the graduations are invisible, rather than to let it run out its course.

they have no signs of addition or subtraction prefixed. Then by tossing up a coin over and over again and calling heads + and tails −, the signs + or − are assigned by chance to this series of errors. About a dozen equidistant values of some function (say sine or cosine) were next taken from a Table, and the errors added to or subtracted from them in order. The errors may be made either small or large by multiplying them by any constant. The falsified values may then be fairly taken to represent a series of observations; but we here know what are the true ones. The corrections were then applied, in some cases arithmetically and in others graphically, and the deviations of the corrected values from the true were observed.

In other cases a series of equidistant ordinates were taken, and a sweeping free-hand curve was drawn to represent the true curve, and the several ordinates of this curve were falsified by the roulette and then corrected by a graphical application of the rule. The general result of a good many trials was such as to justify the smoothing process. Where the errors were considerable the mean error was much reduced, although the actual error of some ordinates was increased; where the errors were very small the mean error was even slightly increased. Although the danger of over-smoothing was obvious, and the sharpness of the features of the curve was generally diminished, yet I think it was clear that the method might generally be employed with advantage, especially in such cases as the attempt to deduce some law from statistics or a series of barometric oscillations of considerable periods. The errors must be very large to justify a quadruple operation. This method of trial could not be so well applied to testing the case of an odd number of smoothing operations, where we are left finally at intermediate ordinates.

On the whole, I think the process is justifiable if applied with caution. Nevertheless it undoubtedly tends to spoil the results if applied to a series of points which are already in a sweeping curve; and therefore I have tried to find some other process which should not have this disadvantage. This can only be done by taking more than three points of the curve into consideration; and therefore the process must be more cumbrous.

The method pursued was as follows:—

Let $-2, y''$; $-1, y'$; $0, y$; $1, y_1$; $2, y_2$ be the coordinates of five consecutive points on the curve. Suppose them to be represented by a curve whose equation is $y = a + bx + cx^2 + dx^3$; and make the following expression a minimum, viz.

$$\Sigma(a + bx + cx^2 + dx^3 - y)^2,$$

where the summation is made for the values of $x=-2, -1, 0, 1, 2$, and the corresponding values of y. In other words, the values of a, b, c, d are to be determined by the method of least squares, so that this curve shall give the best representation of the five points.

The equations for finding a, b, c, d are therefore

$$\begin{aligned} 5a &+ b\Sigma x + c\Sigma x^2 + d\Sigma x^3 = \Sigma y, \\ a\Sigma x &+ b\Sigma x^2 + c\Sigma x^3 + d\Sigma x^4 = \Sigma xy, \\ a\Sigma x^2 &+ b\Sigma x^3 + c\Sigma x^4 + d\Sigma x^5 = \Sigma x^2 y, \\ a\Sigma x^3 &+ b\Sigma x^4 + c\Sigma x^5 + d\Sigma x^6 = \Sigma x^3 y. \end{aligned}$$

From the manner in which the origin has been chosen the sums of the odd powers of x are all zero, and $\Sigma x^2 = 10$, $\Sigma x^4 = 34$, $\Sigma x^6 = 130$.

Thus the first and third equations are

$$\begin{aligned} 5a + 10c &= y'' + y' + y + y_1 + y_2, \\ 10a + 34c &= 4y'' + y' + y_1 + 4y_2; \end{aligned}$$

and the second and fourth may be easily written down. It will be noticed that the first and third equations would be exactly the same if we assumed as the form of the equation $y = a + bx + cx^2$.

Now the proposed method is to substitute for every point of the series of given points the intersection with the ordinate of that point of the curve of the form $y = a + bx + cx^2$ or $y = a + bx + cx^2 + dx^3$ which best represents that point and the two preceding and two succeeding points. In the case we have been considering we are, therefore, to substitute for the the point 0, y the intersection of this curve with the axis of y; that is to say, we are to substitute the point $0, a$, because when $x=0$, $y=a$.

Now $$35a = -3y'' + 12y' + 17y + 12y_1 - 3y_2;$$

or

$$\begin{aligned} a &= y + \tfrac{3}{35}\{-y'' + 4y' - 6y + 4y_1 - y_2\} \\ &= y - \tfrac{3}{35}\Delta^4 y''. \end{aligned}$$

Thus the correction δy, to be applied to y, is $-\frac{3}{35}\Delta^4 y''$.

Hence generally, since the process is supposed to be applied all along the series,

$$\delta y_x = -\tfrac{3}{35}\Delta^4 y_{x-2}.$$

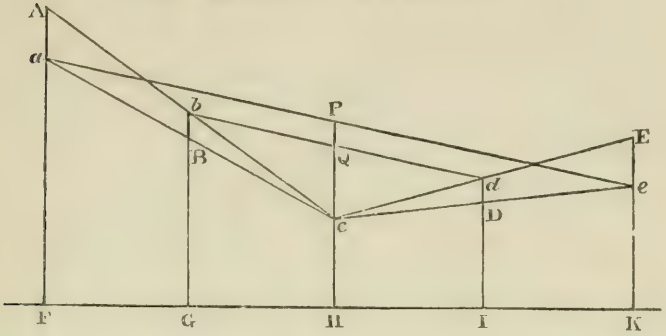
To give a geometrical meaning to the rule, it may be observed that

$$-y'' + 4y' - 6y + 4y_1 - y_2 = -(y'' - 2y + y_2) + 4(y' - 2y + y_1);$$

and therefore if Δ' be a symbol denoting the operation of dif-

ferencing with the omission of alternate ordinates.

$$\delta y_x = \tfrac{12}{35}\left\{\Delta^2 y_{x-1} - \tfrac{1}{4}\Delta'^2 y_{x-2}\right\}^*.$$



Now in the figure let A F, B G, C H, D I, E K be any five consecutive ordinates, and suppose that it is proposed to correct the ordinate C H. Then, if the construction shown in the figure be carried out, it is clear that

$$\text{C P} = \Delta^2(\text{B G}), \text{ and } \text{C Q} = \tfrac{1}{4}\Delta'^2(\text{A F}),$$

and therefore

$$\text{P Q} = \Delta^2(\text{B G}) - \tfrac{1}{4}\Delta'^2(\text{A F}).$$

Thus the correction to be applied to the ordinate H C is $\frac{12}{35}$ (or very nearly $\frac{1}{3}$) of P Q. The same process must be applied all along the series for each set of five points.

Four points are lost out of the series, two at each end. For example, if A, B are the first two points, the rule gives no substituted points on those ordinates. The results obtained from the use of this rule do not seem markedly superior to those given by the empirical method, except where the points lie in a fair curve; and as the rule is more cumbrous to apply, it does not seem likely to be of much practical value.

The construction of a fair surface near a number of points.

The preceding process may be extended to the case where the function involves two independent variables. The observed values may, for the sake of clearness, be considered as consisting of a number of ordinates standing on the intersections of the lines of a chess-board, of which two intersecting edges are the axes of x and y.

Let $[x, y]$ indicate the given ordinate which stands on the

* If the points lie in a fair curve, $\Delta^2 y_{x-1} - \frac{1}{4}\Delta'^2 y_{x-2}$ is very small, a property which I have used to give a rule of graphical interpolation on intermediate ordinates (see the 'Messenger of Mathematics,' January 1877). Thus in this case the correction applied is very small.

point x, y; let E, Δ be the operations of writing $x+1$ for x, and of differencing with respect to x; and let E, D be the like operations with respect to y. Let ϕ represent a single smoothing operation on any series of ordinates which are in a plane parallel to x; and ψ the same with respect to y.

Now apply a smoothing operation ϕ to all the points parallel to x, and then apply the operation ψ to all these new points. The order in which these operations are performed is immaterial; and the result is

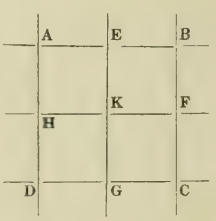
$$\phi\psi[x,y]=\frac{\mathrm{E}^{\frac{1}{2}}+\mathrm{E}^{-\frac{1}{2}}}{2}\cdot\frac{E^{\frac{1}{2}}+E^{-\frac{1}{2}}}{2}[x,y]=\tfrac{1}{4}\{[x+\tfrac{1}{2},y+\tfrac{1}{2}]+[x+\tfrac{1}{2},y-\tfrac{1}{2}]+[x-\tfrac{1}{2},y+\tfrac{1}{2}]+[x-\tfrac{1}{2},y-\tfrac{1}{2}]\}.$$

This, interpreted geometrically, means that we are to erect in the middle of each square an ordinate which is the mean of the four surrounding ordinates. Again,

$$\phi^2\psi^2[x,y]=\tfrac{1}{16}\{[x+1,y+1]+[x+1,y-1]+[x-1,y+1]+[x-1,y-1]+2([x+1,y]+[x-1,y]+[x,y+1]+[x,y-1])+4[x,y]\}.$$

If the figure represents any four squares of the chess-board (in which observe that nine ordinates stand on the intersections), the rule given by a double operation is to substitute for the ordinate at K,

$\frac{1}{16}$ of sum of ordinates at A, B, C, D
+ $\frac{1}{8}$ of sum of ordinates at E, F, G, H
+ $\frac{1}{4}$ of ordinate at K.



It is clear that the operations of smoothing parallel to the two axes are quite independent, and that there is no necessity to smooth the same number of times in each direction. The symbolical way of writing the operation makes it perfectly easy to construct any desired modification of this formula, where ϕ and ψ are each performed any number of times.

The process may also be extended with equal justice to the case where there are three independent variables, although that case no longer admits of geometrical interpretation.

Let t be a third variable; then, if the former notation be extended, and if only a type of each form of term be written down preceded by the sign of summation, it will be found that

$$\phi^2\psi^2\chi^2[x,y,t]=\tfrac{1}{64}\{\Sigma[x\pm1,y\pm1,t\pm1]+2\Sigma[x,y\pm1,t\pm1]+4\Sigma[x,y,t\pm1]+8[x,y,t]\}.$$

There are eight terms of the first kind, such as $[x+1, y-1, t+1]$; twelve of the second, such as $[x+1, y, t-1]$; six of the third, such as $[x+1, y, t]$; and only one of the last, viz. $[x, y, t]$.

Application to Ocean Meteorology.—This last process appears to me to be applicable here. Meteorologists have divided the ocean up into squares of 5° of latitude and 5° of longitude. The logs of ships sailing over those squares are consulted for meteorological observations; and the results are classified by months and squares; and the mean result for any one element, such as the height of the barometer, is taken to be the average for the middle of that square and the middle of that month*. Now it seems as though this were a case where smoothing is justifiable, and that it is allowable to make the result for each month depend in some degree on its neighbours both in space and time. There are three independent variables, viz. latitude, longitude, and time; and in the previous formula we may take these to be represented by x, y, and t respectively.

Suppose, for example, we want to modify the mean height of the barometer for any square e for, say, February, both with reference to surrounding squares and to the heights for January and March. Then the rule for finding the amended height is:—Take the sum of the heights for a, c, g, k for January and for March + twice the sum of the heights for b, d, h, f for January and March + twice the sum of the heights for a, g, c, k for February + four times the sum of the heights of b, d, h, f for February + four times the sum of the heights for e for January and March + eight times the height for e for February, and divide the result by 64.

	a	b	c
	d	e	f
	g	h	k

It must be observed that it is not necessary that the smoothing should be carried to the same extent for x, y, and t. If, for example, we wish to smooth only once for time, the formula will be different, and the result will be applicable to the beginnings of the months instead of the middles. A knowledge of the particular requirements of the case is the only guide to the amount of smoothing which is expedient; but the formulæ are so easy to construct that it does not seem worth while to give any other forms.

In concluding this part of the subject, I may mention that the proposed processes may be extended so as to allow various weights to the various observations.

Terrestrial Meteorology.—There are a number of observa-

* I owe this explanation to Mr. Francis Galton.

tories on the land at which observations are taken at the same hours of the day all over the country; from these results, maps are drawn showing the form of the "isobars" for each day. After the observations have been reduced to the sea-level and corrected in other ways, they may be considered as correct, and the isobars give a graphical illustration of the successive deformations of the barometric surface. Land meteorology serves, then, to give quite a different kind of result from those of ocean meteorology. In the latter the result is the mean heights of the barometer at stated places and times. The oceanic barometric surface, as far as we know it, is ideal, and does not correspond with its real form at any one time. In oceanic meteorology the smoothing process seems justifiable; for we only seek to study the main features of the changes. In land meteorology this is not the case; for we seek to discover the details of the changes. To return to the former metaphor—in one case the law of the waves is sought, in the other the law of the ripples.

The observatories are scattered irregularly over the country; and it seems probable that the results would be more useful and more easily interpreted if they could be distributed at regular intervals of space. They are already regularly distributed as regards time. My present object is, then, to give a formula (which is, as far as I am aware, new) for the reduction of observations scattered irregularly, to regular stations equidistant in latitude and longitude. It is a problem in interpolation of the ordinary kind where the ordinates are not fallible.

The problem is to find a continuous surface passing through the tops of a number of irregularly spaced ordinates; and it may be solved by an extension of Lagrange's well-known formula for interpolation in two dimensions.

Let x_0, y_0; x_1, y_1; &c.; x_n, y_n be the coordinates (latitude and longitude) of a number of points, and let z_0, z_1, &c., z_n be ordinates (barometric heights) corresponding to these points. Lagrange's formula suggests the following as the equation to a surface passing through the tops of z_0, z_1, &c., z_n.

$$z = z_0 \frac{(x-x_1)(y-y_1)(x-x_2)(y-y_2)\dots(x-x_n)(y-y_n)}{(x_0-x_1)(y_0-y_1)(x_0-x_2)(y_0-y_2)\dots(x_0-x_n)(y_0-y_n)}$$
$$+ z_1 \frac{(x-x_0)(y-y_0)(x-x_2)(y-y_2)\dots(x-x_n)(y-y_n)}{(x_1-x_0)(y_1-y_0)(x_1-x_2)(y_1-y_2)\dots(x_1-x_n)(y_1-y_n)}$$
$$+ \&c.$$
$$+ z_n \frac{(x-x_0)(y-y_0)(x-x_1)(y-y_1)\dots(x-x_{n-1})(y-y_{n-1})}{(x_n-x_0)(y_n-y_0)(x_n-x_1)(y_n-y_1)\dots(x_n-x_{n-1})(y_n-y_{n-1})}.$$

Then this formula will give the height z of the barometer at any station whose latitude and longitude are x, y, as deduced from the heights at the several observing-stations. The applicability of this interpolation depends, of course, on the assumption that the surface is not contorted between the given ordinates; and if the observatories are numerous enough, this assumption is probably justifiable.

The application of the formula would in general entail a great detail of arithmetic; but in the case of the reduction from irregular to regular stations, the great mass of the work might be done once for all. In this case the coordinates of the observing stations x_0, y_0; x_1, y_1; &c. are the same day after day, and the coordinates of the fixed stations x, y are constant for each of them. Hence the coefficients of z_0, z_1, &c. in the formula may be calculated once for all.

It would be very laborious and unnecessary to make the heights of the barometer at the equidistant stations depend on all the observatories in the country; and it would be probably quite sufficient to make each one depend on the five or six nearest observatories. The practical rule would then run somewhat in this fashion (the numbers being purely hypothetical):—

Height of bar at lat. $\left.\begin{matrix}\\ 51^\circ \text{ long. } 1^\circ \text{ W.}\end{matrix}\right\}$ = ·705 Oxford + ·20 Kew + ·092 Southampton + ·002 Cambridge.

Every separate point to which the reductions were to be made would require a different set of coefficients, which would depend on the four, five, or six nearest actual observing-stations.

If the heights of the barometer were taken as the excess above 28 inches, the various heights need not be given to more than three figures; and as the coefficients would probably have also three figures, the multiplications might be very easily made by means of Crelle's Rechentafeln. By these means the daily observations might be very quickly reduced, and the results of each day's observations would be given by a series of numbers on a map spaced out at regular intervals of latitude and longitude. This would, I think, facilitate the drawing of the "isobars," and it would also be more intelligible than are the results as given at irregularly dispersed stations.

It may be noticed that the same set of coefficients would also be proper for the reduction of any other meteorological element which could be fairly represented by a surface. The calculation of the coefficients would be rather laborious; but if there is any real advantage in thus classifying the observa-

tions, this would be of slight consequence, as the work would be performed once for all.

In conclusion, I will add one other rule—namely, for interpolation between the oceanic meteorological observations when smoothed, as before suggested. This is a formula for interpolation in the case of a function of three independent variables, the values of which are given at equal intervals, as is the case in the mean barometer-heights in latitude, longitude, and time.

Let Δ, D be the differences between successive barometer-heights in latitude and longitude respectively, and δ the difference in time (that is to say, between the values for successive months). Then, following the former notation,

$$[x+\xi, y+\eta, t+\tau] = [x, y, t] + \xi\Delta + \eta\mathrm{D} + \tau\delta + \frac{1}{1.2}\{\xi(\xi-1)\Delta^2 + \eta(\eta-1)\mathrm{D}^2 + \tau(\tau-1)\delta^2 + 2\xi\eta\Delta\mathrm{D} + 2\eta\tau\mathrm{D}\delta + 2\tau\xi\delta\Delta\} + \&c.$$

The proof of this will be obvious to those acquainted with the Calculus of Finite Differences. No doubt it has been given before, although I do not happen to have met with it. This formula enables us to pass from the regular equidistant values for the middles of squares and months to those for any other neighbouring time and place.

II. *On the Production of Heat by Dynamical Action in the Compression of Gas.* *By the Rev.* J. M. Heath*.

WHEN the equilibrium between the compressive and expansive forces in a given mass of gas has been disturbed by suddenly establishing an arbitrary, but finite, inequality (f) between them, the dynamical effect of this unbalanced force will be, a gradual and continuous alteration in the volume and temperature of the gas, which continues until the expansive force, which depends upon these two elements alone, again becomes equal to that of the compression, and the energy of the inequality is exhausted. At this moment a new condition of equilibrium obtains, in which the elements p', v', t', differ from their former values by determinate finite quantities, δp, δv, and δt.

These quantities will, of course, satisfy the equation

$$v\,.\,\delta p - p'\delta v = pv\,.\,\alpha\delta t,$$

which expresses nothing but that they are the differences of

* Communicated by the Author.

two sets of variables, both of which correspond to a position of equilibrium, the second of which positions may be any whatever. But in the case of our experiment, the second position of equilibrium is absolutely determinate. The only magnitude arbitrarily assumed was the disturbing force f; and that alone has determined the particular values of both δv and δt, for which the disturbance f first becomes equilibrated and replaced by δp. There must be, therefore, a second equation belonging to these three values exclusively, and by combining which with the former any two of the quantities may be determined from the knowledge of the third. This equation, obtained from the experiment itself, was found to be $dv = v.\beta.dt$, where β is a constant quantity. From the two equations $vdp - pdv = pv\alpha dt$ and $pdv = pv.\beta.dt$, we obtain a third, $vdp = pv.(\alpha+\beta)dt$, which gives the increment of temperature corresponding to a given increment of energy.

As an example, let 1 lb. of air at temperature 32° sustain a pressure of 2116 lbs. to the square foot, and occupy a volume $= 12{\cdot}393$ cubic feet, and let an additional weight of f lbs. to the square foot be suddenly put upon it, whereby it is compressed into a volume v' and its temperature is raised to 33°. The value of pv will be in this case 26,224 cubic-foot pounds. The values of α and β now generally received as most accurate, are approximately $\alpha = {\cdot}002$, $\beta = {\cdot}005$, and $\alpha+\beta = {\cdot}007$. Also, since, when $dt = 1°$, $dv = {\cdot}005\, v = {\cdot}062$, and therefore $v' = 12{\cdot}331$, substituting these values, the equation

$$v.dp = (\alpha+\beta)\,pv.dt$$

gives us $vdp = {\cdot}007 \times 26{,}224 = 183{\cdot}6$ cubic-foot pounds; and therefore $f = {\cdot}007p = 14{\cdot}8$ lbs. per square foot, and $p' = 2130{\cdot}8$ lbs., and $p'dv = 132{\cdot}1$ cubic-foot pounds.

Therefore an additional weight of 14·8 lbs. to the square foot, imposed upon the gas already in equilibrium under a pressure of 2116 to the foot, will compress it through ·062 cubic foot, and raise its temperature by 1° F.

To explain this result from thermodynamical principles :— To raise 1 lb. of air by 1° F. a quantity of heat $= {\cdot}2375$ or $\frac{19}{80}$ of unity must have been created. And in this case vdp or 183·6 is the amount of energy which has created it. Therefore $\frac{80}{19} \times 183{\cdot}6$ is the energy which would generate one unit of heat in the gas. But $\frac{80}{19} \times 183{\cdot}6 = 773$ cubic-foot pounds ;—a coincidence with the value obtained by Joule which is truly marvellous, since all the data here made use of were known long before the conception of the dynamical origin of this heat.

The whole energy of the volume of air at 32° was in the first instance $pv = 26224$. But after the condensation and

heating it is $p'v' = 26275$, giving an increase of 51 cubic-foot pounds.

In warming the gas 1° we expended an energy of 183·6 cubic-foot pounds; and if no change had been made in the volume, the energy of the warmer air under the same volume would have been 183·6 greater than that of the cooler. But by the reduction of the volume by ·062 there has been a loss of $·062 \times 2130·8$, or 132·1 cubic-foot pounds, reducing the final gain from 183·6 to 51, which was the actual gain as found above.

No heat has ever been generated in a gas spontaneously and without communication with external bodies, except under the condition of the disturbance of the equilibrium of the forces, as explained above. As long, therefore, as the forces remain in equilibrium (as they do, for example, during the uniform rise or fall of the barometer), any amount of condensation or expansion may take place without affecting the temperature. This is contrary to universal belief. But it is true for all that. It is not from *thermodynamists* that we should have expected to hear that all heat is generated by forces *which are in equilibrium with each other*. This assertion, now, as it is believed, made for the first time, of the existence of what may be called thermostatical condensation and expansion, may be put beyond all doubt by reference to the two equations we established in the beginning of this article, as founded on experience and governing all the cases where heat is really produced dynamically. Those equations were

$$vdp = ·007kdt,$$

$$pdv = ·005kdt,$$

and a third, which may be derived from these two,

$$5vdp = 7pdv.$$

From these it appears that no heat is spontaneously generated in the process of equilibrating a dynamical disturbance—first, in the case where $dp = 0$, secondly where $dv = 0$, and thirdly where $vdp = pdv$, or, indeed, where vdp equals any thing else than 1·4 pdv. That is, no heat is gained or lost by the condensation or expansion of a gas *under constant pressure*, nor by any possible variation of the pressure *while the volume is constant*, nor by any variation of volume and pressure together during which the pressure varies inversely as the volume.

Lastly, it appears from these principles that a gas may be heated during expansion, or cooled during condensation. The equation

$$vdp = ·007ktd,$$

which may be put under the form

$$dp = \cdot 007 \, . \, p \, . \, dt$$

is independent of dv. It expresses that if the equilibrium of the forces is disturbed by a force of seven thousandths of the original pressure, the temperature of the gas will vary 1° F. And this will be the case whatever dv is, *i. e.* whether the gas is condensed or rarefied, much or little. But the same disturbing force produces, simultaneously with the heat, a certain amount of condensation. The equation $dv = \cdot 005 v dt$ proves this. And if the gas was originally not only in equilibrium, but also *quiescent* (that is, neither in a condition of actual expansion nor of condensation), then the effect of the disturbing force will be simply as stated above, to condense the gas. But the gas *may be* in a condition of thermostatic expansion (see above), as for instance the atmosphere about us while the barometer is falling uniformly. If this expansion enlarges the volume in a given time more than the action of the disturbing force condenses it in the same time, the same rise of temperature will take place as before, but the gas will be rarefied. In this case, however, the expansion, as the fall in the barometer, will not be uniform, but *retarded*. So likewise, a gas is cooled during a retarded condensation.

We have shown that by the dynamic employment of the energy $(\alpha + \beta) pv$, the temperature is raised 1° F., and the air is condensed by the quantity βv. Conversely, if the expansive force is suddenly increased beyond the compression in the same proportion, the air will expand itself by βv, and one degree of temperature will be lost and *vis viva* equal to the energy $(\alpha + \beta) pv$ will be gained, either by the rising piston of the engine, or the cannon-ball in the cannon. If this is repeated $\frac{1}{\alpha}$ (=491) times, the air will be deprived of *all* its heat, it will be expanded by $\frac{\beta}{\alpha}$ of its volume, and the cannon ball will have acquired *vis viva* $= \frac{\alpha + \beta}{\alpha} pv$. In the case of 1 lb. of atmospheric air at 32° and barometrical pressure 30 in., this is about 92,000 foot-pounds. This is the *total energy* of the air, being all the *dynamical* work that can be got out of it.

All these consequences of the dynamic theory of heat, are now propounded, as far as I know, for the first time. No account of any one of these cases is given in any existing work on this subject, nor any help to get an answer to such

inquiries as I have here made. I therefore submit them frankly, though not *diffidently*, to the candid judgment of those who are far better qualified than I pretend to be to pronounce upon them. Perhaps the most startling thing I have advanced is that heat is gained and lost in retarded expansions and condensations. But I would ask any thermodynamist how *he* would explain, without this theory, the gain and loss of *vis viva* in the rise of a barometrical column from one point of rest to another, that *vis viva* being, of course, the measure of the loss and gain of heat in the air that generates it. Between two points of rest the motion of the barometer *must be* at first accelerated, and it must be at last retarded; and between these two there *must be* some time when it rose uniformly and the forces were in equilibrium. No *vis viva* has been gained or lost on the whole; but the air has been all the while condensing. What, then, has become of the heat generated?

III. *On the Conditions of Perpendicularity in a Parallelepipedal System. By* H. J. S. Smith, *F.R.S., Savilian Professor of Geometry in the University of Oxford**.

1. THE conception of a parallelepipedal system (*i. e.* of a space divided by three systems of equidistant parallel planes into similar and equal parallelepipeds) may be regarded as forming the basis of the usually received theory of crystallography. It is the object of the present note to state some of the conditions for the perpendicularity of lines and planes in such a system. The results of this inquiry (which has been undertaken at the request of Professor N. S. Maskelyne, and owes much to his suggestions) are submitted to the Crystallological Society with great diffidence, because they do not seem likely to admit of any direct application to the practical work of the crystallographer. Such interest as they possess belongs to a domain which borders on the one hand on pure arithmetic, and on the other hand on pure geometry.

2. It is perhaps hardly necessary to explain that by a "line of the system" we understand a line joining any two points of the given parallelepipedal system, by "a plane of the system" a plane containing three points of the system, the points of the system being the points of intersection of the three sets of equidistant parallel planes by which the system is defined. It will be sufficient to consider *origin*-lines and planes, *i. e.*

* Communicated by the Author, having been read at the Meeting of the Crystallological Society, June 14, 1876.

lines and planes passing through a fixed point of the system taken as origin.

3. Whenever a line of the system is perpendicular to a plane of the system, the system has a certain "symmetry of aspect" with regard to that plane. Let Ω be the plane, and let O be any point of the system lying in it. The planes and lines of the system which pass through O are symmetrically distributed with regard to Ω; but the points of the system are not (in general) symmetrically distributed with regard to Ω: thus, if OP is any line of the system not lying in the plane Ω, and if OQ is the *reflection* of Ω with regard to the plane Ω, OQ is a line of the system as well as OP, but the points of the system which lie on OQ are not (in general) the reflections of the points of the system which lie on OP. Hence, while the points of the system are not themselves symmetrically distributed with regard to Ω, the directions in which they would be viewed by an eye situated at O are symmetrically distributed; and this is what we intend to express by saying that the system has a "symmetry of aspect" with regard to the plane Ω.

As we shall have no occasion in what follows to consider planes of absolute symmetry, we shall for the sake of brevity use the word symmetry in the sense of "symmetry of aspect." Thus any line and any plane of the system which are at right angles to one another are an axis and a plane of symmetry.

4. The cases of symmetry, as thus defined, which can present themselves in a parallelepipedal system are four in number. There is (1) the case of *simple* symmetry, when there is only one axis and one plane of symmetry; and there are three cases of triple symmetry, which may be characterized as (2) the *ellipsoidal*, (3) the spheroidal, and (4) the spherical. In an ellipsoidal system there are three mutually rectangular planes, which are planes of symmetry; in a spheroidal system there is one equatorial plane of symmetry, but every plane of the system at right angles to this plane is also a plane of symmetry; in a system having spherical symmetry every plane of the system is a plane of symmetry, and every line of the system an axis of symmetry. Two simple symmetries cannot coexist without forming a triple symmetry, which is ellipsoidal if the axis of one of the symmetries lies in the plane of the other, but is spheroidal in every other case: three simple symmetries form an ellipsoidal symmetry if the three axes are at right angles to one another, a spheroidal symmetry if one of the axes is at right angles to the plane of the other two which are not at right angles to one another, a spherical symmetry in every other case.

5. Adopting the notation of the classical treatise of Pro-

fessor W. H. Miller, we designate by a, b, c the parameters appertaining to the three lines of the system taken for the coordinate axes; we also denote by X, Y, Z the angles between the coordinate axes, and by X_1, Y_1, Z_1 the angles between the normals to the coordinate planes. We thus have for the square of the distance between any two points of the system the expression

$$f(x,y,z) = a^2x^2 + b^2y^2 + c^2z^2 + 2bcyz\cos X + 2cazx\cos Y + 2abxy\cos Z,$$

where x, y, z denote any positive or negative integral numbers; and this ternary quadratic form may be regarded as characterizing the given parallelepipedal system. Again, if

$$\phi(\xi,\eta,\zeta) = b^2c^2\xi^2\sin^2 X + c^2a^2\eta^2\sin^2 Y + a^2b^2\zeta^2\sin^2 Z + 2a^2bc\eta\zeta\sin Y\sin Z\cos X_1 + 2b^2ca\zeta\xi\sin Z\sin X\cos Y_1 + 2c^2ab\xi\eta\sin X\sin Y\cos Z_1,$$

the form ϕ, which is the contravariant of f, characterizes (in the same way in which f characterizes the given system) a new parallelepipedal system (the polar system of Auguste Bravais) in which every line is perpendicular to a plane of the given system, and in which the parameter corresponding to any line is the elementary parallelogram of the given system lying in the plane to which the line is perpendicular.

6. We write for brevity

$$f = Ax^2 + By^2 + Cz^2 + 2A'yz + 2B'xz + 2C'xy,$$
$$\phi = A_1\xi^2 + B_1\eta^2 + C_1\zeta^2 + 2A'_1\eta\zeta + 2B'_1\xi\zeta + 2C'\xi\eta$$

(so that $A = a^2, \ldots A' = bc\cos X, \ldots, A_1 = b^2c^2\sin^2 X, \ldots A'_1 = a^2bc\sin Y\sin Z\cos X_1, \ldots$); and we observe that, although the five quantities upon which the nature of the parallelepipedal system ultimately depends are the ratios of the parameters a, b, c, and the three angles X, Y, Z, yet the combinations of these quantities which it is most convenient to consider in discussing the conditions of perpendicularity are precisely the six coefficients

$$A, B, C, \quad A', B', C',$$

and the six contravariant coefficients

$$A_1, B_1, C_1, \quad A'_1, B'_1, C'_1.$$

Thus the condition that the lines of the system

$$\left.\begin{aligned} \frac{x}{au} &= \frac{y}{bv} = \frac{3}{cw}, \\ \frac{x}{au_1} &= \frac{y}{bv_1} = \frac{3}{cw_1}, \end{aligned}\right\} \quad \ldots\ldots \quad \text{(i)}$$

should be perpendicular to one another is

$$u_1\frac{df}{du}+v_1\frac{df}{dv}+w_1\frac{df}{dw}=0,$$

or

$$u\frac{df}{du_1}+v\frac{df}{dv_1}+w\frac{df}{dw_1}=0;$$

the condition that the planes of the system

$$\left.\begin{aligned}\frac{hx}{a}+\frac{ly}{b}+\frac{kz}{c}&=0,\\ \frac{h_1x}{a}+\frac{l_1y}{b}+\frac{k_1z}{c}&=0\end{aligned}\right\}\quad\ldots\ldots\quad\text{(ii)}$$

should be perpendicular to one another is

$$h_1\frac{d\phi}{dh}+k_1\frac{d\phi}{dk}+l_1\frac{d\phi}{dl}=0,$$

or

$$h\frac{d\phi}{dh_1}+k\frac{d\phi}{dk_1}+l\frac{d\phi}{dl_1}=0;$$

and the conditions that the first of the lines (i) should be perpendicular to the first of the planes (ii) may be written in one or other of the equivalent forms

$$\frac{\left(\frac{df}{du}\right)}{h}=\frac{\left(\frac{df}{dv}\right)}{k}=\frac{\left(\frac{df}{dw}\right)}{l},$$

$$\frac{\left(\frac{d\phi}{dh}\right)}{u}=\frac{\left(\frac{d\phi}{dk}\right)}{v}=\frac{\left(\frac{d\phi}{dl}\right)}{w}.$$

7. Let us now suppose that the given parallelepipedal system contains a pair of perpendicular lines (i); the condition of perpendicularity gives immediately

$$\begin{aligned}&Auu_1+Bvv_1+Cww_1+A'(vw_1+wv_1)+B'(wu_1+w_1u)\\&\quad+C'(uv_1+u_1v)=0.\end{aligned}$$

Unless, therefore, the six covariant coefficients are connected by a linear homogeneous relation having integral coefficients, no two lines of the system can be perpendicular to one another; and correlatively, unless the six contravariant coefficients are connected by a similar relation, no two planes of the system can be perpendicular to one another. But the existence of such a relation connecting the six covariant coefficients (or the six contravariant coefficients), though a necessary condition, is

not a sufficient condition for the existence of a pair of perpendicular lines or planes. We proceed, therefore, very briefly to describe the principal cases which present themselves when the coefficients are connected by one, two, three, four, or five linear relations. By a linear relation connecting the coefficients we understand a linear homogeneous equation of the type

$$p\mathrm{A}+q\mathrm{B}+r\mathrm{C}+2p'\mathrm{A}'+2q'\mathrm{B}'+2r'\mathrm{C}'=0,$$

where p, q, r, p', q', r' are integral numbers which we may suppose free from any common divisor. In connexion with such a relation we shall have to consider the quadratic form

$$\psi=p\xi^2+q\eta^2+r\zeta^2+2p'\eta\zeta+2q'\zeta\xi+2r'\xi\eta$$

and its contravariant or reciprocal form

$$\Psi=(p'^2-qr)x^2+(q'^2-rp)y^2+(r'-pq)z^2+2(pp'-q'r')yz \\ +2(qq'-r'p')zx+2(rr'-p'q')xy.$$

These we shall term the quadratic form and the reciprocal quadratic form appertaining to the given relation. For brevity we shall attend only to the cases in which given relations exist between the six covariant coefficients A, B, C, A′, B′, C′, the cases in which given relations exist between the six contravariant conditions being simply the correlatives of these. It is remarkable that in every case the conditions of perpendicularity and symmetry depend solely on the coefficients of the linear relations connecting the crystallographic coefficients; so that two parallelepipedal systems, in which the crystallographic coefficients have different ratios but satisfy the same linear relations, would resemble one another exactly in respect of symmetry and perpendicularity.

8. *Case of one linear relation between the coefficients.*

Here we have the theorem, "The system contains a single pair of perpendicular lines, or contains no such pair whatever, according as the reciprocal form appertaining to the given relation is or is not a perfect square."

For the condition that the reciprocal form Ψ should be a perfect square, we may if we please substitute the condition that the quadratic form ψ appertaining to the given relation should resolve itself into two rational factors. Or, again, we may replace this condition by the two conditions. (1) that the discriminant of ψ is to be zero, (2) that the greatest common divisor of the first minors of this discriminant is to be a perfect square.

9. *Case of two linear relations between the coefficients.*

We represent the quadratic forms and the reciprocal quadratic forms appertaining to these relations by $\psi_1\Psi_1$, $\psi_2\Psi_2$,

and by $\theta, \theta', \theta''$ the roots of the discriminantal cubic of $\psi_1 + \theta\psi_2$. If these roots are irrational, the system contains not a single pair of perpendicular lines. If one of them, for example θ, is rational, we still have to examine whether the factors of $\psi_1 + \theta\psi_2$ are rational; if they are, we have a pair of perpendicular lines. If all the three roots $\theta, \theta', \theta''$ are rational, we have to examine the factors of each of the three forms $\psi_1 + \theta\psi_2$, $\psi_1 + \theta'\psi_2$, $\psi_1 + \theta''\psi_2$; according as these factors are or are not rational (if the factors of two of them are rational the factors of the third are so too), we obtain one or three pairs of perpendicular lines, or no pair at all of such lines.

When two of the roots $\theta, \theta', \theta''$ are equal, we have either one, and only one, pair of perpendicular lines; or we may have two pairs, the plane of one of the right angles containing one of the rays of the other right angle. When the three roots are all equal we have a single pair of perpendicular lines.

Lastly, the coefficients of the discriminating cubic may all vanish. If this happens, either (α) Ψ_1 and Ψ_2 differ, if at all, by a numerical factor, and every line of the system that lies in a certain plane has a line of the system at right angles to it in the same plane; or (β) ψ_1 and ψ_2 have a common linear factor, and the system possesses a simple symmetry.

We may thus enunciate the theorem:—

"The conditions that a parallelepipedal system should possess a simple symmetry are (a) that the coefficients should be connected by two linear relations, (b) that the two quadratic forms appertaining to these relations should have a linear factor in common."

10. *Case of three linear relations between the coefficients.*

We represent by ψ_1, ψ_2, ψ_3 the quadratic forms appertaining to the given relations, and we obtain the following theorem:—

"The system contains no right angle, or an infinite number, according as the indeterminate cubic equation

$$C = \begin{vmatrix} \frac{d\psi_1}{d\xi}, & \frac{d\psi_1}{d\eta}, & \frac{d\psi_1}{d\zeta} \\ \frac{d\psi_2}{d\xi}, & \frac{d\psi_2}{d\eta}, & \frac{d\psi_2}{d\zeta} \\ \frac{d\psi_3}{d\xi}, & \frac{d\psi_3}{d\eta}, & \frac{d\psi_3}{d\zeta} \end{vmatrix} = 0$$

does or does not admit of solution in integral numbers."

By virtue of the three given relations the characteristic ex-

pression $f(x, y, z)$ of art. 5 assumes the form

$$f(x, y, z) = \omega_1 f_1 + \omega_2 f_2 + \omega_3 f_3,$$

the ratios of the quantities ω_1, ω_2, ω_3 being irrational, but the coefficients of the quadratic forms f_1, f_2, f_3 being integral numbers. If $H(x, y, z)$ denote the Jacobian of these three forms, we have the theorem:—

"When the indeterminate equation $C = 0$ admits of solution, the infinite number of right angles which the system contains all lie on the cubic cone $H(xa, yb, zc) = 0$; viz. an infinite number of lines of the system lie on this cone, and every line of the system which lies on it has a line at right angles to it, also lying on the cone."

The system may have a simple symmetry or an ellipsoidal symmetry, or none at all; but it cannot have a spheroidal or a spherical symmetry.

The conditions for a simple symmetry are that the ternary cubic form $C(\xi, \eta, \zeta)$ should resolve itself into a rational linear factor and a rational quadratic factor, and that the ternary cubic form $H(x, y, z)$ should resolve itself into three linear factors. These conditions admit of being further developed (see Dr. Salmon's 'Higher Plane Curves,' pp. 190 and 202 *seqq.*); it is sufficient for our purpose to observe that the coefficients of the Jacobian $H(x, y, z)$, no less than those of $C(\xi, \eta, \zeta)$, depend solely on the coefficients of the forms ψ_1, ψ_2, ψ_3, *i. e.* on the integral numbers entering into the given linear relations.

The conditions for an ellipsoidal symmetry are that $C(\xi, \eta, \zeta)$ should resolve itself into three rational linear factors, and that $H(x, y, z)$ should resolve itself into three factors.

Two special cases of the general theory (which, however, are not cases of symmetry) deserve attention.

(1) There may exist in the parallelepipedal system a quadratic cone and a plane, such that every line of the system lying in the plane has a line of the system at right angles to it lying in the cone.

(2) Or, again, the parallelepipedal system may have an infinite number of pairs of perpendicular lines all lying in the same plane; and it may also have at the same time a second set of such pairs lying on the surface of a quadratic cone, the plane of each pair of this second set passing through the polar line of the first-named pair with regard to the cone.

11. *Case of four linear relations between the coefficients.*

Here every line, without exception, of the parallelepipedal system has a line at right angles to it; and this distribution of pairs of perpendicular lines may exist without the presence of any symmetry whatever. The symmetry (if any) may be simple, or ellipsoidal, or spheroidal, but cannot be spherical.

The characteristic form $f(x, y, z)$ may be expressed by an equation of the type

$$f = \omega_1 f_1 + \omega_2 f_2,$$

the ratio of ω_1 and ω_2 being irrational, but the coefficients of the quadratic forms f_1 and f_2 being integral numbers. There is a simple symmetry when the discriminantal cubic of $f_1 + \theta f_2$ has one rational root, an ellipsoidal symmetry when it has three rational and unequal roots, a spheroidal symmetry when it has two equal roots. (It cannot have its three roots equal, because the cone $f(x, y, z) = 0$ is imaginary.)

We suppress the further discussion of these conditions, only observing that they may be so expressed as to show that they depend only on the coefficients of the four given relations, and not on the six coefficients A, B, C, A′, B′, C′ themselves.

12. *Case of five linear relations between the coefficients.*

In this case the ratios of the coefficients are themselves evidently rational, and the parallelepipedal system has a spherical symmetry. It is also true, conversely, that when there is a spherical symmetry the ratios of the coefficients are rational.

We may mention that the question of the rationality or irrationality of the ratios of the crystallographic coefficients had attracted the attention of Gauss, who, as appears from the memoir of his life (Gauss, *Zum Gedächtniss*, von W. Sartorius v. Waltershausen: Leipzig, 1856), had in the year 1831 devoted himself with great ardour to the study of crystallography*.

IV. *Notes on the Theory of Sound.* *By* R. H. M. Bosanquet, *Fellow of St. John's College, Oxford.*

[Continued from vol. iii. p. 424.]

5. *On the Symmetrical Spherical Divergence of Sound in Air.*

THE principal interest of this subject, from a practical point of view, is its bearing upon the reflexion of sound at its divergence from the end of a tube. I hope to return to a more particular examination of this question on a subsequent occasion; in the present note I shall allude to it only so far as is necessary to make intelligible the interest of the results obtained in the restricted case here dealt with.

The investigations of Helmholtz on the divergence of sound from the open end of a cylindrical tube (*Crelle*, 1860), broke ground for the first time in the knowledge of the manner in

* Some of the demonstrations, which have been omitted in the present note, will be found in a paper inserted in the 'Proceedings of the London Mathematical Society,' vol. vii. p. 83.

which sound actually passes over from the inside of a tube into the surrounding air. The work was based on the modern potential analysis; and some of the chief difficulties in it were overcome by giving to the various expressions the meaning they would have had in the theory of electricity, and employing the results that belong specially to that theory.

Lord Rayleigh treated important portions of the same subject in a paper in the Philosophical Transactions, 1871 (Mr. Strutt "On Resonance"). The analysis is much simplified, but it is essentially the same in principle as Helmholtz's. The reference to electrical analogies is used freely.

A paper by Grinwis (Pogg. *Ann.* 1877, No. 2, p. 276) goes over that portion of the ground which refers to resonators; it does not appear to me to differ essentially in principle from the papers already mentioned.

When sound diverges from the end of a cylinder, the motion is such as it would be if the cylinder were made a little longer and the process of divergence were disregarded. The principal numerical result, the obtaining of which is the object of theory, concerns the magnitude of the length supposed to be added to the cylinder as the equivalent of the divergence. The whole space considered is always supposed to have its dimensions small compared with the wave-length.

The electrical method is defective in the view it affords of the actions which take place, in a manner which I will endeavour shortly to explain.

In Bernoulli's theory of organ-pipes, the hypothesis is made that the change from the constraint of the pipe to a condition in which no remains of constraint are to be perceived takes place suddenly at the point where the wave-system leaves the pipe. This theory is useful as a first approximation, but entirely fails to give any idea as to the connexion between the motion in the pipe and that in the surrounding air. It is, however, evident that the divergence which takes place may be conceived of as sending back to the pipe a series of reflected impulses, instead of the single reflected impulse which returned from the open end of the pipe according to the Bernoulli theory, and that these elementary impulses, coming from different distances, may be together equivalent to a single reflected impulse from a point at a little distance from the end of the pipe. The position of the source of this equivalent disturbance may be called the "centre of phase" of the reflected wave-system; and in its relation to the series of elementary systems, as well as in the formulæ by which it may be found, it has a striking analogy to the centre of gravity of a system of material points.

The electrical method entirely puts aside all consideration of reflexion; and between it, as exhibited by Helmholtz and his followers, and the Bernoulli theory there exists a want of connexion. It will be my endeavour to extend the Bernoulli theory in the direction above indicated, so as to arrive (in the present note by the application of rigorous analysis to the case of symmetrical divergence, and in the following note with the assistance of the experimental study of the unsymmetrical motions concerned) at a more clear idea of the whole thing than was afforded by the electrical analogies.

Preliminary Illustration.—Reflexion by Change of Section.

If a stream of sound traverse a cylinder whose section changes from S_0 to S_1, a reflected stream will arise at the change of section—the change of section being small, and the wave-length great compared with the dimensions of the section; so that the form of the plane-waves is substantially undisturbed, and the expansion may be considered as taking place completely in the plane of the section.

Let A be the amplitude of the incident stream,
b of the transmitted stream,
a of the reflected stream.

Let MS_0A^2 be the energy per second of the incident stream,
MS_1b^2 of the transmitted stream,
MS_0a^2 of the reflected stream.

By Prop. II. of the last note, the incident and reflected streams in S_0 do not interfere with each other.

Let the axis of the cylinder be the axis of x, and its intersection with the plane of change of section the origin. Then the wave-systems may be represented by

$$y_0 = \mathrm{A}\sin k(vt-x) + a\sin k(vt+x),$$
$$y_1 = b\sin k(vt-x).$$

We suppose that the whole reflexion takes place at the change of section, so that no change of phase comes into the reflected system except π, which is determined by the sign of a. This is legitimate as long as the change of section is small. Then

$$\frac{dy_0}{dx} = -k\mathrm{A}\cos k(vt-x) + ka\cos k(vt+x),$$

$$\frac{dy_1}{dx} = -bk\cos k(vt-x).$$

And these must be equal at the origin ($x=0$); for the pressure must be the same at the common surface;

$$\therefore\ \mathrm{A}-a=b.$$

And the reflected and transmitted energy per second together = incident flow;

$$\therefore\ S_0A^2 = S_1b^2 + S_0a^2.$$

From these equations we find, rejecting the solution $b=0$,

$$b = 2A\frac{S_0}{S_1+S_0},\quad a = A\frac{S_1-S_0}{S_1+S_0},$$

which determine the reflected and transmitted streams.

It is easy to treat similarly the more general case, where two streams flowing in opposite directions meet at the change of section; but the form of analysis is not convenient for proceeding much further, so I pass on.

We may deduce from the above the general principle, that if (under the conditions stated) a stream of sound-energy diverge, occupying at successive instants a variable surface S, portions of the energy will be reflected back at every instant; and since the total amount is constant (conservation of energy), the total amount on surface S diminishes as the surface increases. If we suppose it uniformly distributed over the surface, we may then express the total energy on S in the form*

$$E = E_0 + \frac{E_1}{S} + \frac{E_2}{S_2} + \dots,$$

where E_0, E_1, E_2 are coefficients depending on the circumstances. There can be no positive index terms, since the energy supplied cannot augment itself.

If S change to $S+dS$, E changes to $E-dE$; and since dE is not sent forward, it is reflected back. Hence the general expression for the reflected element of energy is

$$dE = E_1\frac{dS}{S^2} + 2E_2\frac{dS}{S^2} + \dots.$$

In the cases I shall consider, the first term alone is important; it would be possible to found subsequent developments very simply on the first term of the above expansion. But it is desirable to discuss the case of spherical divergence more fully.

* In the case where the surface S diminishes as the stream flows on, the expression is different: since the energy per second through successive surfaces S cannot increase, negative powers are excluded; and the expressions in the text are replaced by

$$E = E_0 + E_1S + E_2S^2 + \dots,$$
$$dE = (E_1 + 2E_2S + \dots)dS,$$

where dS is the element of diminution of surface.

Symmetrical Spherical Divergence.

The simplest case of the divergence of sound is where it issues from a spherical source, and spreads symmetrically in all directions. This may be realized by supposing a small sphere, pierced with holes like the rose of a watering-pot, to be connected through a long tube with a source from which air alternately issues and is abstracted, the tube being thin enough not to interfere sensibly with the spherical divergence. Of course also the conditions are the same in hemispherical or sectorical divergence, the sound diverging always from a corresponding portion of a spherical surface. In these cases the assumption that R, the velocity-potential, is a function of r and t only, is legitimate, but in no other case.

If we form the equations of motion in three dimensions in the ordinary manner, making the above assumption, we have (Airy, 'On Sound,' p. 92)

$$\frac{1}{v^2}\frac{d^2\mathrm{R}}{dt^2}=\frac{d^2\mathrm{R}}{dr^2}+\frac{2}{r}\frac{d\mathrm{R}}{dr}.$$

There are three principal forms of integral of the above equation with which we are concerned:

$$\mathrm{R}=\frac{\mathrm{C}\sin k(vt-r)}{r}, \quad \ldots\ldots\ldots \quad \text{(i)}$$

$$\mathrm{R}=\frac{\mathrm{C}\sin k(vt+r)}{r}, \quad \ldots\ldots\ldots \quad \text{(ii)}$$

$$\mathrm{R}=\frac{\mathrm{C}}{r}, \quad \ldots\ldots\ldots\ldots \quad \text{(iii)}$$

The corresponding velocities are,

(i) $$\frac{d\mathrm{R}}{dr}=-\frac{\mathrm{C}}{r^2}\{kr\cos k(vt-r)+\sin k(vt-r)\},$$

(ii) $$\frac{d\mathrm{R}}{dr}=\quad\ _{r^2}\{kr\cos k(vt+r)-\sin k(vt+r)\},$$

(iii) $$\frac{d\mathrm{R}}{dr}=-\frac{\mathrm{C}}{r^2}.$$

In (i), (ii) of the values of $\frac{d\mathrm{R}}{dr}$ the coefficient $kr=\frac{2\pi r}{\lambda}$; if λ be regarded as indefinitely great with respect to r, the last terms alone survive, and the velocities reduce to

$$\text{(i)} \quad -\frac{C}{r^2}\sin k(vt-r),$$

$$\text{(ii)} \quad -\frac{C}{r^2}\sin k(vt+r),$$

$$\text{(iii)} \quad -\frac{C}{r^2}.$$

The expression for the density is (Airy, p. 67)

$$D\left(1-\frac{1}{v^2}\frac{dR}{dt}\right),$$

which gives for the variable terms deduced from R,

$$\text{(i)} \quad -DC\frac{kr}{v}\cos k(vt-r),$$

$$\text{(ii)} \quad -DC\frac{kr}{v}\cos k(vt+r),$$

$$\text{(iii)} \quad 0.$$

The terms of variable density in (i) and (ii) bear the same analogy to the first terms in their complete velocities that the densities of ordinary sound-waves of transmission do to the corresponding velocities; but if we suppose kr small, these changes of density are negligible compared with those that would be required to correspond to the surviving terms of the velocities. And ultimately, when the velocity $=\frac{C}{r^2}$, there is no change of density at all, and we may regard the fluid as incompressible under the circumstances.

This once admitted, in the case where the wave-length is supposed very great in comparison with all the dimensions considered, we can deduce the whole motion very simply from other considerations in the important case where the velocity $=\frac{C}{r^2}$ or there is a uniform flow—the limiting case when the wave-length is infinite.

Let S_0 be the surface of the spherical source, $S_0 dr$ the volume of fluid that flows through S_0 in the time dt; then

$\frac{dr_0}{dt}=V_0$ is the rate of flow of fluid through S_0,

$\frac{dr}{dt}=V$ through S.

Since the fluid is continuous and of constant density (according to the above reasoning), the same quantity of fluid crosses

every surface S in the same time dt; $\therefore S dr = \text{const.}\, dt$, and

$$SV = S_0 V_0.$$

The energy of the flow under these circumstances lying between surfaces S_0 and S, is

$$\frac{\rho}{2}\int_{r_0}^{r} V^2 S dr = \rho \frac{V_0^2 S_0^2}{2}\int_{r_0}^{r} \frac{dr}{4\pi r^2}$$
$$= \rho \frac{V_0^2 S_0^2}{8\pi}\left(\frac{1}{r_0} - \frac{1}{r}\right).$$

When r becomes great in comparison with r_0, the last term ceases to influence the expression. Consequently the energy of the whole motion lying beyond such a value of r is negligible in comparison with that which lies within it; or if we make r indefinitely great, the energy has the finite value ($S_0 = 4\pi r_0^2$)

$$2\pi\rho r_0^3 V_0^2.$$

None of this passes off to infinity; consequently the maintenance of the motion when once started requires no additional expenditure of energy (of course friction is neglected). Hence we have the curious theorem, that if an infinite mass of frictionless fluid be set in symmetrical divergence in the manner indicated, as soon as steady motion has set in no further pressure is required from the supply-channel, but if the fluid is brought to the surface of the small sphere from which divergence takes place it will be drawn out, and the motion continued, by means of the energy already present.

I will now endeavour to analyze more closely the course taken by the flux of energy in this problem, and to illustrate the mechanical action by which this last result is produced.

We may suppose the energy to be divided into two streams, both accompanied with outward velocity of displacement. The one is divergent; it has a greatest pressure inside, and a less pressure towards the outside. The other is convergent; and it proceeds inwards with continually increasing rarefactions.

If we combine these two streams in the same way as the two opposite streams of sound which make up a stationary wave (see Prop. I. of note 4), the velocities are both equal to $\frac{V}{2}$ at any point, and the condensations are

$$+\frac{V}{2r} \text{ for the divergent wave,}$$

and

$$-\frac{V}{2r} \text{ for the convergent wave.}$$

The total energy per second across the surface is

$$\frac{\rho v S V^2}{2},$$

or

$$\frac{\rho v}{2}\frac{V_0^2 S_0^2}{S} = \frac{K}{S} \text{ say,}$$

that of each of the component streams into which it is above decomposed being half this amount, $= \frac{K}{2S}$, where

$$K = \frac{\rho v}{2} V_0^2 S_0^2.$$

Consider the divergent stream which starts from S_0, and has the energy per second $\frac{K}{2S}$ as it passes through each surface S. As the divergence proceeds elements are reflected; and the element reflected in expansion from S to S+dS is

$$dE = \frac{K}{2}\frac{dS}{S^2}.$$

These reflected elements would probably diverge in turn but for the symmetry; all we can say here is that the actual motion is represented by treating them as forming a convergent stream.

Summing the reflected elements, then, from any value of S up to an infinite value, we have for the total reflected energy (numerically) $\frac{K}{2S}$, the same value as that of the divergent stream at the point.

Hence the motion of spherical divergence in air is completely represented by decomposing the motion into a divergent and a convergent stream of energy, the latter of which is made up of the reflected elements of the former. And the mechanism by which the maintenance of the flow is continued when once started, as proved above, is the suction exerted at the source S_0 by the reflected convergent stream of energy, which is accompanied with rarefaction.

This really amounts to making a supposition that the constraint terminates at S_0, a supposition which cannot be actually realized, involving a Bernoulli reflexion of the rarefaction into pressure at S_0. Supposing a pipe to be terminated by two such spherical divergences, the air flowing inward at the one end and outward at the other, the convergent rarefaction would travel along the tube to the other end, whence issuing as a divergent

rarefaction it would be reflected into a convergent pressure by a process exactly the reverse of the above; this would in turn reenter the pipe, travel back to the first source S_0, and begin the cycle afresh. This would be a simple case of a stream-line in an indefinitely extended frictionless fluid, the flow through which would be maintained, by circulation of energy, when once started. Such spherical divergence, however, cannot be actually set up at the end of a tube with any approach to accuracy.

In considering the energy of the motion, we saw that the amount of it which lies beyond a distance r from the centre is negligible when r is great in comparison with r_0. This remark becomes important subsequently, when it will illustrate the extremely small influence on numerical results of great differences in the ultimate forms of motion at great distances. But we shall employ the remark now to illustrate the passage from the case of uniform flow of fluid to that of a periodic flow, represented by a circular function, according to solutions (i) or (ii) of the differential equation.

Instead of the velocity V being uniform, suppose it to be a function of the time, such as $V \sin kvt$, where $k\ (=\frac{2\pi}{\lambda})$ is small with respect to distances at which the energy is sensible. We cannot suppose this as it stands to satisfy the conditions for a flow of energy. But if we notice that, kr and kc being small, $\cos k\,(r-c)$ differs indefinitely little from 1, we can put this function $= V \sin kvt \cos k(r-c)$, where c denotes an arbitrary origin; we see that we now have a motion analogous to that in the neighbourhood of a loop surface with plane-waves, which may be referred to the two streams of sound-energy

$$\frac{V}{2} \sin k(vt-r+c)$$

and

$$\frac{V}{2} \sin k(vt+r-c)$$

(Prop. I. of note 4). The energy per second of each stream will be $\frac{\rho v V^2}{8}$, and that of the two together twice this amount, or half that in the case of continuous motion.

Although I am going to prove this rigorously presently, yet the derivation by the reasoning just employed is important, because we shall want it later in an analogous case; so I will say a few words more on the details.

The deduction of the distribution of energy required only

that the fluid should behave as if incompressible (which I assume throughout as a consequence of the analysis), and that the motion should at the instant of examination be the same as if a steady flow were going on. This happens when a definite value is ascribed to t, the velocity anywhere being then $\frac{V_0 S_0}{S} \sin kvt$. This being the case, the equation of continuity is satisfied, and the rest of the reasoning runs as before. The total energy at any instant is found by multiplying the preceding result by $\sin^2 kvt$ (coefficient of V^2), and is

$$2\pi\rho r_0^3 V_0^2 \sin^2 kvt.$$

The observations made on the former result are true also of this; none of it lies at an infinite distance. Where, then, does it go to for the values of t for which $\sin kvt$ approximates to zero? The answer is, that this sort of motion can only exist in combination with some other form capable of receiving the energy and converting it either into another form of kinetic, or into potential energy, as it disappears from the motion we are considering. The simplest case is that of a resonator. If we imagine a large vessel full of air to be connected with the outer air by a system of spherical divergence of this kind, the total energy in use is exchanged between the moving air and the store expressed by the compression or rarefaction in the vessel. The analysis of the energy into two streams corresponding to those employed in the case of constant flow has been already exhibited.

To turn to the analytical side of the question.

It is not in general sufficient, for a form of motion to be a solution of a problem, that it should satisfy the differential equation of the second order to which the problem is subject. It must also satisfy the energy-conditions, and also in any particular case the conditions imposed by the initial circumstances. Examples of this are found in the limitations on the superposition of plane-wave systems travelling in the same direction, which are discussed in Props. III. *et seqq.* of the last note.

Now, if we turn to our integrals of the differential equation of symmetrical spherical divergence, we might say, if we overlooked the above considerations, that (i) alone was an integral of the equation and a possible form of motion, and that the form to which it reduces when kr is very small is also a possible form, *i. e.* that a possible motion is capable of being expressed by a velocity

$$-\frac{C}{r^2} \sin k(vt-r).$$

Now this term signifies a transmission of energy outwards at the rate of

$$\frac{\rho v}{4}\frac{C^2}{r^4} \text{ per second per unit surface ;}$$

that is to say, the energy through surface πr^2 gradually diminishes in the ratio of $\frac{1}{r^2}$: it disappears ; there is nowhere for it to go to. It is clear, therefore, that this is not a solution as far as the flow of energy is concerned.

It is only necessary to take up integral (ii), and out of (i) and (ii) to combine a solution which shall be consistent with the energy-conditions. Of course the origin of r is so far indeterminate, as well as the origin of time. We here introduce a constant c ; and the following is the expression for the resulting velocity, deduced as a combination of integrals (i) and (ii) of the differential equation of symmetrical spherical divergence :—

$$\text{velocities } \frac{V_0 S_0}{2S}\sin k(vt-r+c) \text{ divergent,}$$

$$\frac{V_0 S_0}{2S}\sin k(vt+r-c) \text{ convergent,}$$

which combined give the velocity of a region in the neighbourhood of a loop surface,

$$\frac{V_0 S_0}{S}\sin kvt\cos k(r-c),$$

or, since $k(r-c)$ is small,

$$\frac{V_0 S_0}{S}\sin kvt;$$

that is to say, the differential equation is satisfied by the motion of a stationary wave near its loop (therefore unaccompanied by changes of density), and the energy-conditions are satisfied by representing it as the sum of a divergent and a convergent stream.

It remains to show how either of the component streams may be regarded as made up of the elements of energy reflected from the other at the different surfaces S. It is easy to see that the result of such a number of reflexions may be represented by supposing them collected into one reflexion at a distance r from the centre. In the expressions for the divergent and convergent velocities put $c=\bar{r}$; then the position denoted by $\bar{r}$ will correspond to the actual loop surface of the stationary

wave, and the velocities become :—

$$\text{divergent} = \frac{V_0 S_0}{2S} \sin k(vt - r + \bar{r}),$$

$$\text{convergent} = \frac{V_0 S_0}{2S} \sin k(vt + r - \bar{r}),$$

both of which become $\frac{V_0 S_0}{2S} \sin kvt$, if $r = \bar{r}$.

Now the transmission of energy takes place with the velocity of sound ; so that the consequence of the loop being at a distance $\bar{r}$ from the centre is that the reflected system is later in phase than it would have been if reflected all at once at S_0, by the time sound takes to travel over $2(\bar{r} - r_0)$.

For convenience in estimating this retardation, let us alter our origin of time in the above equations by the time sound takes to travel over $\bar{r}$; the equations become :—

$$\text{divergent velocity} = \frac{V_0 S_0}{2S} \sin k(vt - r) ;$$

$$\text{convergent velocity} = \frac{V_0 S_0}{2S} \sin k(vt + r - 2\bar{r}).$$

The first is now in a form independent of the reflexion ; and the latter expresses the features of a wave reflected at a distance $\bar{r}$ from the centre. If we regard this latter stream as made up of elements of energy per second reflected from the successive surfaces traversed by the former, we have for the velocity-element reflected from distance ρ ($V' =$ maximum velocity of reflected vibration $= \frac{V}{2}$),

$$[dV' \sin k(vt + r - 2\rho).$$

Expanding this expression, and remembering that $k\rho$ is small, we have

$$dV'\big(\sin k(vt + r) - 2k\rho \cos k(vt + r)\big).$$

If these elements are all transmitted to S_0, as is indicated by the original equations, so as to make up there the reflected velocity across S_0, this becomes

$$V'_0 \sin k(vt + r) - 2k \int_{r_0}^{\infty} \rho dV'_0 \cos k(vt + r);$$

and if we put

$$\int_{r_0}^{\infty} \rho dV'_0 = r \int_{r_0}^{\infty} dV'_0 = \bar{r} V'_0),$$

the total velocity of the reflected stream at S_0 is expressed in the form

$$V'_0 \sin k(vt + r - 2\bar{r}).$$

And the reflected stream is determined in phase in a manner which is represented by supposing it to originate wholly at a distance $\bar{r}$ from the centre, where $\bar{r}$ is defined by

$$\int_{r_0}^{\infty} \rho dV'_0 = \bar{r} \int_{r_0}^{\infty} dV'_0.$$

The energy per second of the reflected stream at S_0 is

$$\frac{\rho v V'^2_0 S_0}{2} = E_0.$$

If we suppose this quantity to be varied by the abstraction of the energy-element per second reflected at surface S,

$$dE = \rho v V'_0 \, dV'_0 \, S_0.$$

The energy per second of the divergent stream through surface S is

$$\frac{\rho v}{8} \frac{V_0^2 S_0^{2*}}{S} = \frac{K}{4S};$$

and the element reflected at distance r from the centre is

$$\frac{K dS}{4S^2} = dE,$$
$$= \rho v S_0 V'_0 \, dV'_0;$$

and $2V'_0 = V_0$;

$$\therefore dV'_0 = \frac{V_0 S_0}{4} \frac{dS}{S^2}.$$

The reflected stream is then determined in phase by the equations

$$\int_{r_0}^{\infty} r \frac{dS}{S^2} = \bar{r} \int_{r_0}^{\infty} \frac{dS}{S^2} = \frac{\bar{r}}{S_0};$$

and if $S = 4\pi r^2$,

$$r = 2r_0;$$

that is to say, the reflected stream is the same in phase as if it came from a single reflexion, at a distance beyond S_0 equal to its radius r_0.

We can employ this at once to get an approximation to Helmholtz's result for hemispherical divergence from the end

* Prop. I., cor., of Note 4. The total energy per second in periodic flow = that in constant flow, *if the periodic flow be that of an ordinary stream with pressures and velocities.* In these loop-surface motions with velocities only, the total energy per second in terms of the velocity is half that in the case of constant flow or in the case of an ordinary transmitted sound-wave.

of a cylinder. (Helmholtz makes the correction $=\frac{\pi}{4}\mathrm{R}$, where R is the radius of the open end. Lord Rayleigh has shown that this is a lower limit, and regards the real value as about ·82 R.) Assuming that the divergence depends chiefly on the surface values, represent the circular end of the cylinder $\pi\mathrm{R}^2$ by S_0, a hemisphere of equal surface, described about the centre of $\pi\mathrm{R}^2$; then, if $\mathrm{S}_0=2\pi r_0^2$, $r_0=\frac{\mathrm{R}}{\sqrt{2}}$. The reflected wave reenters this hemisphere as if reflected from a distance $=r_0$ beyond its surface; so that the correction to the length of the pipe would be $\frac{\mathrm{R}}{\sqrt{2}}=\cdot 707\,\mathrm{R}$, as against the value $\frac{\pi}{4}\mathrm{R}$ and ·82 R above mentioned.

The transformation from the circle to the hemisphere of equal area is only admissible as an approximation; but for this purpose it is valuable, as the whole reasoning admits of being stated very shortly.

The problem of spherical divergence is interesting as illustrating the precision of ideas attaching to the present method, compared with that based on electrical analogies; for, so far as I am aware, it is not possible to obtain, or even to imagine, any strictly corresponding result in the electrical theory. Consider the case of the divergence of electricity from a spherical surface through a conducting medium indefinitely extended. Then, according to the analogy formerly applied, the resistance to the diverging current furnishes the quantity analogous to the retardation in the sound-problem. This resistance is easily found, from the consideration that it is proportional to the thickness, and inversely as the surface, of each successive spherical layer. And

$$\int_{r_0}^{\infty}\frac{dr}{4\pi r^2}=\frac{1}{4\pi r_0}.$$

Similarly for a hemisphere, total external resistance $=\frac{1}{2\pi r_0}$.

This result has been interpreted by supposing a cylindrical tube, of radius r_0, to be capped with a hemisphere, from which the divergence takes place. If l be the length of the tube equivalent to the resistance of divergence, σ the section of the tube,

$$\text{resistance}=\frac{l}{\sigma}=\frac{1}{2\pi r_0},$$

and

$$\sigma = \pi r_0^2 ;$$

$$\therefore\ l = \frac{r_0}{2}.$$

Another interpretation may be obtained by supposing the tube to have a section equal to the surface of the hemisphere. Under these circumstances we find $l = r_0$, a result numerically the same as that of our direct investigation. It is, however, clear that the electrical resistance does not, in this case at least, really represent any thing strictly analogous to r (which we may call the "distance of centre of phase") in the direct investigation; for the latter subsists in the case of the spherical divergence itself, but it is impossible to assign any similar meaning to the electrical result while the spherical form is maintained. In the case of unsymmetrical divergence the law is different; for the reflected energy diverges so that only a portion of it reaches the initial surface.

According to the motion above investigated, on the contrary, the whole of the reflected energy returns in the reflected stream; a tube terminated by such a divergence would consequently, in a frictionless fluid, be a perfect resonator, from which no energy would be lost in steady vibration, so far as this divergence is concerned. As, however, symmetrical spherical divergence cannot be actually set up with any approach to accuracy, it is impossible to check the theory in this manner. The trumpet-shaped mouths of wind-instruments, however, probably cause some approximation to this type of motion.

To allude only to the question whether sound varies inversely as the square of the distance, we notice that, under the conditions of spherical divergence with great wave-length, the total energy per second $\propto \frac{1}{S}$; consequently the energy per second through unit surface $\propto \frac{1}{S^2}$, or $\propto \frac{1}{r^4}$. But at great distances from the source, or when the distance is great compared with the wave-length, the motion is that of an ordinary transmitted wave-system whose total energy per second through surface S is constant; so that at such distances the energy per second on unit surface does vary inversely as the square of the distance.

In the next note I shall attempt to deal with unsymmetrical divergence, such as that from the ends of organ-pipes, and shall discuss the experimental treatment of this part of the subject.

V. *On the Application of Thermodynamics to the Study of the Variations of Potential Energy of Liquid Surfaces.* By G. Van der Mensbrugghe, *Correspondent of the Royal Academy of Belgium*. Second Preliminary Communication.*

In my first communication† I proposed to determine the quantity of heat dQ gained or lost by a liquid mass of which the surface S receives an increment dS. Representing by T the potential energy of the unit of surface at the absolute temperature t, and neglecting every other cause of variation in the energy of the body, I found the equation

$$dQ = A t d\left(S\frac{dT}{dt}\right); \quad . \quad . \quad . \quad . \quad . \quad (1)$$

and having applied it successively to various particular cases, I then deduced from it the transformed equation

$$id\tau = d\left(S\frac{dT}{dx}\right), \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

which gives the intensity i of the current corresponding to the quantity of heat dQ by which the surface S is traversed in the time $d\tau$, x being the difference of electric level.

As I have already said, the surface S may represent either the free surface of a liquid, or the surface of separation of two liquids which do not mix, or the surface of contact of a solid and a liquid.

On the present occasion I will suppose that we give to the temperature t of the unit of weight of a liquid an increment dt, which will necessarily produce an increase dS of the surface. Since this augmentation dS develops a variation of heat dQ (expressed above), I shall be able to write, designating by K the specific heat as given by experiment at the temperature t, and by k the specific heat as it would be at this temperature if the surface had no potential energy,

$$Kdt = kdt - A t d\left(S\frac{dT}{dt}\right). \quad . \quad . \quad . \quad . \quad (3)$$

According to this equation, the specific heat K would be a function not only of the temperature t, but also of the surface S of the liquid and of the potential energy T of this surface.

* Translated from a separate impression, communicated by the Author, from the *Bulletins de l'Académie Royale de Belgique*, 2e série, tome xli. No. 7, July 1876.

† *Bulletins de l'Académie Royale de Belgique*, 2e série, t. xli. p. 769; Phil. Mag. [V.] vol. ii. p. 450, December 1876.

We thus see how the ideas first expressed by M. Weber*, and quite recently by M. Walthère Spring†, according to which "the variations of specific heat follow the variations of volume of bodies by heat," would be justified. Moreover the value of K would be composed of two parts:—one, k, depending at once on the temperature, the volume, and the pressure; the other a function of t, S, and T. Now it is conceived that a body may have very different surfaces for one and the same initial volume; hence it follows that, for large values of S, the variations of k will be very slight in comparison with those of the second term, which depends on S and T. We shall by-and-by see a very curious consequence of this deduction.

I will now apply equation (3) to the examination of various questions of general physics, upon which my theory appears to throw a bright light.

I. Let us suppose, in the first place, that the variations of S are very inconsiderable and can be neglected pending the variations of the temperature t; then formula (3) becomes

$$\mathrm{K} = k - \mathrm{A}t\mathrm{S}\frac{d^2\mathrm{T}}{dt^2}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

In truth we do not at present know the exact form of the function which expresses T by means of t for any liquid whatever; but we can at least, for a given liquid, seek the values of the coefficients of an equation such as

$$\mathrm{T} = \alpha + \beta t + \gamma t^2 + \ldots .$$

Now it follows from the researches of M. Wolf that, for water, the coefficients β and γ are very small and permit us to neglect the powers of t higher than the second. Besides, for the same liquid, $\frac{d^2\mathrm{T}}{dt^2}$ is negative; from this it follows that the quantity of heat to be supplied to or taken away from the unit weight of water, to raise or lower the temperature 1°, in general increases not only with t, but also with S. Consequently, if we imagine a sphere of water weighing 1 kilogram, and a series of n spheres of water of which the total weight is also equivalent to 1 kilogr., it will be necessary to supply or withdraw much more heat to raise or lower the temperature 1° in the series of n spheres than in the single sphere; and the difference will be by so much the greater as the globules shall be more numerous and consequently more

* "Ueber die specifische Wärme fester Körper, insbesondere der Metalle," Pogg. *Ann.* vol. xx. p. 177.

† "Sur la dilatation, la chaleur spécifique des alliages fusibles," &c., *Bull. de l Acad. Roy. de Belgique*, t. xxxix. p. 548.

minute. Is not this the reason that, according to the observations of Saussure and Fournet, the minute drops forming clouds and mists can float in the strata of air whose temperature is much below zero, without assuming the solid state?

What has just been said of a series of n globules weighing together the unit of weight applies equally to each isolated drop; in fact, if V represents the volume, and δ the specific gravity of the liquid forming the drop, we have

$$K = k - \frac{At S \frac{d^2T}{dt^2}}{V\delta}.$$

Now the ratio $\frac{S}{V}$ increases as the volume of the drop diminishes; and consequently, since $\frac{d^2T}{dt^2}$ is negative, the smaller the diameter of the drop the greater will be the value of K. Does not this explain how M. Mousson* was able, at very low temperatures, to keep in the liquid state globules of water of less than $\frac{1}{2}$ millim. diameter disposed upon a surface which they did not wet? In the same way Mr. Tomlinson †, more than thirty-five years since, could see minute drops of water, alcohol, ether, roll upon the surface of a fixed oil raised to more than 200° C.

In the case where T designates, not the potential energy of a free liquid surface, but that of a surface common to two liquids which do not mix, similar effects to the preceding can be obtained. Thus M. L. Dufour ‡ obtained globules of water in the liquid state immersed in a mixture of chloroform and oil, although the temperature descended as low as −10° C., and even −20° for the smallest spherules. He verified still more marked effects with globules of fused phosphorus or sulphur in the midst of a liquid of the same density.

If the question be of the surface of contact of a solid and a liquid which wets the latter, we shall have to ascertain the sign of $\frac{d^2T}{dt^2}$, in order to foresee the quantity of heat necessary to a variation of potential energy in the surface of contact; if the sign be negative, we must again conclude that K also increases with the surface S. Now a great number of experi-

* "Sur la fusion et la solidification de l'eau," *Bibl. Univ. de Genève*, 1858, t. iii. p. 296.

† Student's Manual of Natural Philosophy, p. 553.

‡ "Sur la congélation de l'eau et sur la formation de la grêle," *Bibl. Univ.* 1861, t. x. p. 346.

ments show precisely this result. I will cite a few examples in support of the last conclusion.

1. If the solid wetted by the liquid has its maximum density and consequently its minimum surface, the specific heat is itself a minimum at this point, and takes a greater value on both sides of the temperature of maximum density. This was proved by M. Spring, by a very elegant mode of experimentation, for the alloys of Rose and Darcet immersed in oil *. But in the immediate vicinity of the maximum anomalies may present themselves, on account of the eventual change of sign of $\frac{dT}{dt}$; this, again, was observed by the same physicist for the above alloys; I shall return to it a little further on.

2. We know how water resists congelation when it is enclosed in capillary spaces, and to what degree organized bodies can support severe cold with impunity because their fluids are enclosed in vessels of microscopic minuteness. In these cases the contact-surface between the solid and the liquid, relatively to the volume of the latter, is enormous.

3. But the present theoretic deduction is confirmed in an unexpected manner by the remarkable experiments of the eminent physicist M. Melsens †, relative to the truly astonishing quantity of heat necessary to detach a volatile liquid from the surface of a very porous substance such as wood-charcoal. Permit me to cite one of those experiments. 23 cubic centims. of sulphide of carbon are introduced into a Faraday tube containing 30 grams of charcoal; the long branch, containing the charcoal, is introduced into a tin tube filled with water, which is slowly brought to ebullition; the short branch of the first tube dips into a freezing-mixture which is kept between 15° and 17° C. below zero. Under these conditions the water must be heated for more than an hour, in order to collect 2 or 3 cubic centims. of sulphide of carbon in the short branch.

4. Lastly, I will mention a very curious property of gun-cotton covered with a very inflammable liquid (for example, benzine, ether, sulphide of carbon, &c.) and exposed to the action of the electric spark: the liquid alone ignites; the gun-cotton does not explode.

II. Let us now suppose t invariable, and see what quantity of heat must be supplied to cause the surface S to vary between the limits S_1 and S_2. If Q denote this quantity of heat,

* "Sur la dilatation, la chaleur spécifique des alliages fusibles," &c., *Bull. de l'Acad. Roy. de Belgique*, 1873, t. xxxix. p. 548.

† "Notes chimiques et chimico-physiques, 5e note," § "De la tension des liquides volatils au contact du charbon," *Mém. Couronnés et autres Mém. publiés par l'Acad. Roy. de Belgique*, t. xxiii.

we shall then have :—

$$dQ = -Atd\left(S\frac{dT}{dt}\right) = -At\frac{dT}{dt}dS\ ;$$

$$Q = -At\frac{dT}{dt}(S_2 - S_1). \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Therefore the quantity of heat to be supplied or withdrawn varies proportionally to the fresh surface produced, $S_2 - S_1$.

This theorem can easily be applied to some well-known phenomena, such as the ebullition of liquids and the fusion of solids.

1. When the temperature of a boiling liquid remains nearly stationary, the liquid is traversed by an infinity of bubbles, the limiting surfaces of which possess a potential energy that increases in proportion to their extent ; each bubble therefore grows larger only by cooling the liquid ; so that the mass must be constantly heated to counteract this cooling. To this cause of production of cold must be added further the renewal of the bounding surface of each bubble, which arises from the volume comprised within each bubble becoming saturated with vapour. Accordingly we conceive that the ebullition will be the more active (that is to say, the greater number of bubbles will be formed) the more heat is supplied in the same time.

I will add that if, for want of air dissolved in the liquid or adhering to the sides of the vessel, all formation of fresh surfaces within the liquid is rendered difficult if not impossible, the temperature of the mass rises more and more, and far beyond that which corresponds to regular ebullition ; in fact, since the beautiful and celebrated experiments of M. Donny*, we know to what an elevated temperature one can bring a liquid, without making it boil, when the air has been expelled from it as much as possible.

My theory explains with equal clearness the fall of temperature, sometimes considerable, which is always experienced at the time of a sudden explosion of vapour-bubbles in a liquid heated beyond its normal boiling-point ; with respect to this I may refer to the curious experiments of the English physicist Professor Tomlinson†. Thus my formula confirms the idea enunciated long since by Donny, and afterwards verified by Dufour, that, in order to produce regular ebullition, it suffices to pass through the liquid a very light current of any gas whatever.

* "Mémoire sur la cohésion des liquides et sur leur adhérence aux corps solides," *Mém. Cour. des Savants étrangers de l'Acad. Roy. de Belg.* t. xvii.

† "On some Phenomena connected with the boiling of liquids," Phil. Mag. 1875, vol. l. p. 85.

Conversely, if the free liquid surfaces disappear at the time of the condensation of the vapour, the potential energy of which those surfaces were the seat vanishes, but is found again in the form of heat sensible to the thermometer. To me the preceding theory appears to show perfectly the origin and the nature of the latent heat of vaporization; indeed, taking for our starting-point the incontestable existence of the potential energy of a free liquid surface, we have arrived by calculation at this result—that every enlargement of the surface develops cold, as every diminution or suppression of a free surface will give rise to a production of heat.

2. In the second place, when a solid body is brought to a temperature sufficient to effect its fusion, the surface of contact of the already fused layer and the yet solid nucleus possesses negative potential energy; that is to say, if it is destroyed cold is produced. Now, with every fresh layer melted, the primitive contact-surface is replaced by another which is necessarily smaller; and consequently there will be cooling, if the heat supplied be not sufficient to compensate this effect. It is evident that the fusion will be by so much the more active the more quickly the heat supplied can replace one contact-surface by another smaller.

Conversely, when solidification takes place, there are also formed successive surfaces of contact between the solid and the still liquid material; but in this case, instead of going on diminishing, the surfaces grow larger and larger, and must consequently produce a progressive heating. It is thus that formula (5) renders intelligible the origin of the latent heat of fusion.

III. Let us now suppose that S and t vary simultaneously, as generally happens; we shall then necessarily have the combination of the two preceding effects (I. and II.); only, as we may easily convince ourselves, the influence of the surface will far exceed that of the temperature. As examples in connexion with the present hypothesis I may cite the evaporation of liquids, the phenomena referred to the spheroidal state, the solution of solids in liquids, &c.

I shall not dwell upon these different instances, because, after what has been said above, the formula can be applied with great facility; but I will endeavour to account for a surprising fact recently studied by M. Spring*, concerning the variations of the specific heat in the neighbourhood of the maximum of density of certain bodies.

Rose's alloy, immersed in an oil-bath, is gradually cooled from 118°. The temperature falls rapidly to the point at

* See the memoir already cited.

which solidification commences ; there it maintains itself, and then rises again a fraction of a degree, ending by decreasing very rapidly until the alloy passes through its maximum density ; at this point the temperature *reascends* about 7°, and this in spite of the cooling, and then descends, following a regular course. Darcet's alloy exhibits similar phenomena.

M. Spring concludes from these singular facts that it is impossible to determine the specific heat even at the temperature of the maximum density, since, notwithstanding the cooling, the temperature rises a considerable quantity. Now this is how, in my theory, I succeed in explaining in a very simple fashion these anomalies, so contrary to all received ideas, presented by the alloys of Rose and Darcet, as well as by others :—

Let us resume our equation (3), and apply it successively to the three temperatures t', t'', t'''—of which the first designates a temperature a little above that of the maximum density, the second that of the maximum density itself, and the third a temperature a little below t''; we can then, accentuating in the same way the corresponding values of K, k, S, and T, and supposing a negative change of temperature (that is, a cooling) as in M. Spring's experiments, write:—

$$-\mathrm{K}'dt' = -k'dt' + \mathrm{A}t'd\left(\mathrm{S}'\frac{d\mathrm{T}'}{dt'}\right);$$

$$-\mathrm{K}''dt'' = -k''dt'' + \mathrm{A}t''d\left(\mathrm{S}''\frac{d\mathrm{T}''}{dt''}\right);$$

$$-\mathrm{K}'''dt''' = -k'''dt''' + \mathrm{A}t'''d\left(\mathrm{S}'''\frac{d\mathrm{T}'''}{dt'''}\right).$$

Now, as I have said above, the variation of the term which depends on the surface may, at least starting from pretty large values of S, be regarded as notably higher than that of k. Under these conditions the sign of the observed specific heat K would be precisely the same as that of the term containing S and $\frac{d\mathrm{T}}{dt}$. But at the maximum of density each of the two terms of the second member cancels itself ; in fact, since the volume passes to the minimum, the quantity $\pm k''dt''$ of heat to be supplied to cause the body to pass from the point which immediately precedes or follows the volume at the minimum itself must be *nil*. As for the term which is a function of S, on the one hand the surface S passes through a minimum to the point we are considering ; on the other, the potential energy T'' passes through a maximum (neglecting its sign) ; for the molecules of the alloy immersed in the oil are then

closer together than on one side or the other of the maximum of density; hence it follows that $\frac{d\mathrm{T}''}{dt''}=0$, and that consequently $d\left(\mathrm{S}''\frac{d\mathrm{T}''}{dt''}\right)$ is in like manner $=0$. It results from this reasoning that the quantity $d\left(\mathrm{S}\frac{d\mathrm{T}}{dt}\right)$ will change sign in passing through the maximum, and that, if for example the sign of that quantity is positive immediately before the maximum of density, it will become negative after passing through the latter. Therefore suppressing the terms in k' and k''' as too small to change the sign of the second member, and representing by α and β the absolute values of K′ and K‴, we shall have:—

$$-\mathrm{K}'\,dt'=\mathrm{A}t'd\left(\mathrm{S}'\frac{d\mathrm{T}'}{dt'}\right)=-\alpha dt';$$

$$-\mathrm{K}''\,dt''=0;$$

$$-\mathrm{K}'''dt'''=\mathrm{A}t'''d\left(\mathrm{S}'''\frac{d\mathrm{T}'''}{dt'''}\right)=+\beta dt''';$$

whence

$$\mathrm{K}'=\alpha,\quad \mathrm{K}''=0,\quad \mathrm{K}'''=-\beta;$$

that is to say, the specific heat is positive at a temperature immediately above that of the maximum density, zero at the maximum, and negative at a temperature below but very near it.

It would be very easy to show how the temperature, after reascending in spite of the cooling, soon stops, and ends by descending again. For this, we have only to admit that the variables S and T soon satisfy the condition,

$$\mathrm{S}\frac{d\mathrm{T}}{dt}=\text{a constant};$$

from that time the differential $d\left(\mathrm{S}\frac{d\mathrm{T}}{dt}\right)$ becomes again $=0$, and a new change of sign is effected in the value of K.

If my demonstration were precise, one could perfectly comprehend the anomalies just spoken of. It will be remembered that in my first communication I noticed some peculiarities of the same kind, observed by M. Jungk in the vicinity of the maximum of density of water: in this liquid, when absorbed by sand, there is a heating if the initial temperature is higher than $+4°$ C., while a cooling is produced if that temperature is below $+4°$ C.; in like manner there is a diminution of temperature when water at 0° is absorbed by snow. These results would be explained in an analogous manner to the preceding.

I consider it a very fortunate circumstance that observers have met with facts so abnormal in appearance, because these latter give a valuable support to my theory. In reality, the character of the maximum or minimum of the expression $S\frac{dT}{dt}$ for particular values of S and t necessarily involves two effects of contrary signs on this side and on that of this particular state of the body. It hence follows that, if physicists had not already noted the striking irregularities of which I have spoken, my theory might have instigated their discovery.

IV. If the consequences which I have deduced from my formula be verified not only by the facts already known, but moreover by the experiments which it may suggest, it can be foreseen of what importance this theory will be in thermodynamics, in which the state of a body is at present regarded as determined when the volume, the temperature, and the pressure supported by the body are given. When a liquid, and very probably also when a solid or a gaseous body, is in question, it will be absolutely necessary to take account of the potential energy which prevails in all the bounding surfaces.

The investigation of this question will be able to be carried on step by step, in proportion as facts shall have brought more confirmation to the calculations which have served me as a basis for the deduction of the various consequences enunciated in my two communications.

V. I should now have to investigate what are the electrical phenomena corresponding to the various developments of heat which have been in question in this note ; but this is too wide a subject for any thing less than a special treatise. I will, for the present, only say that, from the numerous bibliographical researches which I have already instituted, I hope to find for my theory a confirmation as complete in the domain of electricity as in that of heat.

VI. *On the Chromatic Aberration of the Eye in relation to the Perception of Distance. By* Silvanus P. Thompson, *B.A., B.Sc.**

1. THE experimental researches of Wollaston, Arago, Fraunhofer, Young, Matthiesen, Brewster, Müller, and Helmholtz have left no doubt that the eye has the defect of chromatic aberration. Rays of light of dissimilar colour, starting in the same direction from any luminous point and

* Communicated by the Author, having been read before the Physical Society, May 12, 1877.

entering the eye, do not all come to focus upon the retina at once, but the foci for differently coloured rays are differently situated with respect to the retina.

Hence, so far as the perception of the distance of a luminous object is dependent upon the accurate focusing of rays upon the retina of the eye, so far the want of adjustment in the eye introduces a source of error into the data of our perception. If the eye be not achromatic, a blue object and a red object of equal dimensions placed side by side cannot be in focus at once, and hence must appear either unequally distant or else of unequal magnitude.

2. The object of this paper is to demonstrate that the fact thus briefly sketched out affords a true and legitimate explanation of certain empirical rules of artistic practice relative to the pictorial expression of distance. The existence and universal recognition of such empirical rules has presented itself as a problem to the mind of the writer for the past six years; but it is only within the last few months that the solution now offered has been adopted by him.

It is proposed therefore :—

I. To enumerate the various data dependent on the eye and not upon the feet or other limbs, for the formation of a perception of distance.

II. To discuss the weight to be attached to the several data under various circumstances.

III. To inquire how far these data may be dependent upon the apparent colour of an object, or upon the formation of an exact focus upon the retina of the eye.

IV. To give a brief account of some experimental results, together with conclusions derived therefrom.

I. *Data for the Perception of Distance.*

3. The following nine data may be enumerated as contributing to the formation of a perception of distance.

4 (*a*). Apparent motion of objects caused by motion of the observer. If we move from one place to another, or alter the position of the head, the visible configuration of objects suffers a corresponding change, which by association with previous experience suggests an external system, of whose distance this "parallax" affords us an idea.

5 (*b*). Apparent change of configuration of objects according as they are viewed with one eye or the other. This affords a "parallax" similarly to (*a*), though on a more limited scale.

6 (*c*). The muscular sensation of convergence or divergence of the two eyes when directed towards an object. This is a genuine muscular perception, though guided by the optical

perception of want of positional adjustment when the corresponding parts of the two images do not fall upon the corresponding points of the two retinæ.

7 (*d*). Retinal magnitude of an object as appreciated by the muscular effort of turning the eyeball so as to bring the parts of the image successively into the centre of the field of vision.

8 (*e*). Retinal magnitude as a sensation of excitement of a certain area of nerve matter of the retina.

9 (*f*). The muscular sensation of effort of the ciliary muscle in the adjustment of the eye to exact focus. The perception of exactness or inexactness of focus which guides the muscular action is, too, an optical effect in itself of little value as a means of estimating distance, except in so far as it controls the required muscular contraction.

10 (*g*). Binocular dissimilarity of the images on the two retinæ, which, conspiring to give one mental impression, present slight differences that suggest the idea of distance.

11 (*h*). Linear perspective. Under this term I propose to include, beside the usually understood play of lines and diminishing apparent magnitudes commonly spoken of as perspective, such artificial means of estimating distance as are afforded by comparison with objects of known size (figures, cattle, &c.), and such notions of position, surface, &c. as can be drawn from comparison with houses or other objects of known form and magnitude.

12. (*i*) *Aerial Perspective*, in its widest sense. On this point Helmholtz has most aptly remarked* that the brain has the same means for the appreciation of relative distance as are employed by the painter on his canvas; and he enumerates amongst these means strong shadows, bold relief in the foreground, obscurity of atmosphere, and dimness of outline, in addition to contrasts with objects of known size or form. The term, however, is often restricted to the peculiar alteration of the colour of objects due to the intervening atmosphere †.

II. *Relative Importance of foregoing Data.*

13. It is obvious that the considerations advanced in (*a*), (*b*), and (*c*) are foreign to the present inquiry, though of

* 'Popular Lectures,' English edition, p. 281.

† Mr. Ruskin's definition of aerial perspective is, from an artistic point of view, of value. "Aerial perspective is the expression of space by any means whatsoever, sharpness of edge, vividness of colour, &c. assisted by greater pitch of shadow, and requires only that objects should be detached from each other by degrees of intensity in *proportion* to their distance."—'Modern Painters,' vol. i. p. 139.

enormous importance in the estimation of distances in general; for there can be no doubt that where these means are available, the mind is guided to a large extent by them in the formation of an estimate of distance, unless carefully trained to disregard them and to depend on other circumstances, or unless, as may happen to individuals, some physical injury has occurred to render the eye abnormal. With respect to the consideration advanced in (*c*), I have some reason to doubt whether we really do judge apparent distance by the muscular sensations of the external and internal recti muscles of the eye. Stereoscopic pictures appear to me equally "solid" whether in a Wheatstone's reflecting stereoscope, a Brewster's lenticular with prism-shaped lenses, or a Helmholtz's with parallel axes, or by superimposition by effort of the recti muscles, in each of which cases a different convergence is required. Moreover it would be very inconvenient if our estimate of distance depended on the action of these muscles, as they are peculiarly liable to fatigue.

14. Retinal magnitude, to use the term adopted by Wheatstone, whether regarded in its muscular (*d*) or its optical (*e*) sense, affords only an indirect means of estimating distance by association with ideas previously acquired concerning the retinal dimensions of objects of known size at known distances. Nothing is more easy than deception arising from this cause. We constantly hear the magnification of the telescope spoken of as though the enlargement of the retinal image produced the same effect as if the object were brought so near to the eye as to yield a retinal image of equal area. This is evidently not the case, as the distant object, however much magnified in the telescopic image, is still seen by rays travelling in paths nearly parallel to each other, and not containing angles as great as those contained by rays proceeding from an object really near. Hence a telescopic presentation of an object is flatter than the object itself appears when brought sufficiently near to give a retinal image of equal magnitude.

15. The fallacy of judging distances by apparent magnitude is made evident by the absurd comparisons often made between the sun or moon and other objects, some individuals comparing them to the size of a coin, a plate, or a cart-wheel. Comparatively few persons could at once tell you correctly which appears the larger, the setting sun or a threepenny-piece held at arm's length—the fact being that the angular magnitude of the latter exceeds that of the former.

16. The following experiment* illustrates a remarkable

* My attention was first drawn to this curious fact by Mr. Joseph Beck, of the eminent firm of Smith and Beck.

power of accommodation of the eye to the requirements of the mind in respect of retinal magnitude. Place under a stereoscope a penny and a halfpenny, having the "heads" of both coins placed upwards and similarly. You shall see but *one* coin when looking with the two eyes, especially if you expect no dissimilarity and do not use the eyes alternately. There are, on the other hand, experiments of Helmholtz, Fechner, and Volkmann* which go to prove that the retinal magnitude, as appreciated by the muscular sweep of the eye, affords a fairly accurate means of comparison of the angular magnitudes and positions of two objects in the field of vision whose images can be successively brought upon the same spot of the retina. This involves, however, the question of the persistence of visual impressions, without which such a comparison of retinal magnitudes might be quite fallacious.

17. The sensation (f) of tension of the ciliary muscle is a very delicate means of estimating near distances, and is a sensation capable of training to a considerable nicety. In October 1870 the writer was unable to perceive any difference of strain of adjustment to vision between distances of 4 yards and 400 yards. At the present time he is conscious of a difference of tension when the eye is directed to objects 15 yards and 300 yards distant respectively, and this with either eye. I insist on this means of estimation of distance, because it is, for monocular vision, of even more importance than the muscular sensation of convergence of the optic axes is for binocular vision.

18. The researches of Wheatstone, Brewster, Dove, Helmholtz, Brücke, Müller, Rood, Volkmann, and Wundt upon the stereoscopic presentation of objects resulting from the binocular dissimilarity of the two retinal images (g) illustrate the importance of this fact of binocular vision. Wheatstone's pseudoscope proved the point by a *reductio ad absurdum*; and an equally conclusive proof is obtained by cutting a stereoscopic slide in two and placing the halves in laterally reversed position under the stereoscope. I have, however, experimentally found that considerations of colour may sometimes outweigh the judgment founded by the eye upon the element of dissimilarity. I drew a pattern of two squares of four blue lines each upon paper, and within each, and outside each, centrally described circles in red. When this pattern was viewed in the stereoscope, the blue squares seemed to draw back from the eye. I then traced some of Möser's crystal forms from the well-known lithographed stereoscopic slides, colouring the

* Helmholtz, 'Popular Lectures,' p. 279; and *Physiologische Optik*, pp. 522–524 and 542.

front lines of the crystals with ultramarine, and the *back* lines with vermilion. Several, though not all, of these when placed in the stereoscope refused to appear of their true form, the blue lines, whose positions would stereographically give a front presentment, retiring behind the red lines of the crystal.

That the mind does, however, habitually make use of the dissimilarity of binocular vision is evident from the old trick of looking with one eye through a short tube while attempting to walk up to a suspended ribbon and cut it with a pair of scissors. Yet persons who have the use of but one eye find no difficulty in performing the task; and, with practice, the feat becomes easy if the distance be carefully estimated by the sensations of ocular focus. The linear distance between the two eyes, however, sets a limit to the range of habitual estimates of distance founded on the fact of binocular dissimilarity; and, as Mr. Ruskin has observed*, it is possible to see, and to see in focus together, the extreme distance and the middle distance of a landscape, though the foreground and distance cannot so be seen together.

19. I cannot here dwell upon questions involving linear perspective (*h*). The various considerations upon which linear perspective becomes a basis for the perception of distance are purely associative—mental rather than optical, geometrical rather than physical.

20. I pass on, therefore, to aerial perspective (*i*); the various definitions of which may be summed up in one as the expression of distance by colour. A distant hill looks bluer than a less distant one by reason of the slight opacity of the intervening atmosphere ("sky"); and its blueness is in some manner, to a normal eye, a far truer measure of its distance than any one of the considerations yet treated of. The blueness thus existing in nature varies with the changing conditions of atmosphere, and hence is liable to be fallacious when the atmospheric conditions are unfamiliar. Thus in Smith's 'Optics' it is narrated of Bishop Berkeley that, when travelling in Italy and Sicily, he thought the cities as he approached them two or three miles too near, by reason of the unfamiliar transparency of the air.

* Mr. Ruskin advances this point in defence of the practice of landscape-painters in leaving foregrounds sketchy and unfinished, maintaining that they should exhibit "a decisive imperfection, a firm but partial assertion of form which the eye feels indeed to be close home to it, and yet cannot rest upon, nor cling to, nor entirely understand, and from which it is driven away of necessity, to those parts of distance on which it is intended to repose."—'Modern Painters,' vol. i. pp. 183 and 184, note. Mr. Ruskin adds that Turner was the first to introduce this treatment into landscape art.

III. *Bearing of Chromatic Aberration upon the foregoing Data.*

21. Taking the chromatic aberration of the eye as an established matter *, it is now time to inquire how far these various considerations are affected by the fact that rays of different colours have different focal length in the eye.

22. Obviously all estimates of distance which depend on retinal magnitude are liable to be influenced by colour. This may easily be verified by taking two equal disks of red and blue paper and placing them upon a black background. It will be found impossible to get a perfectly distinct image of both at once, one or other being out of focus, and therefore blurred at the edge and larger; or if no difference in size appears, one (the blue one) will appear more distant. The experiment may be varied by giving various sizes and shapes to the coloured disks, but with the same result, especially if the disks be looked at with one eye only. Orange and green disks may answer the purpose, but not so well as disks of red and blue, as these colours are most widely separated on the spectrum†.

23. On this account I am disposed to think that retinal magnitude has little to do with the appreciation of distance, except in the case of objects whose magnitude and tint are familiar to us; and I shall show other reasons for the opinion. Hence I regard as very imperfectly true the statement of the late Sir Charles Wheatstone, in the Bakerian Lecture for 1852 ‡, that "Convergence of the optic axes therefore suggests fixed distance to the mind; variation of retinal magnitude

* In 1835 Brewster wrote: "I consider the *non-achromatism of the eye* as a fact as well established as any other fact in natural philosophy,' Phil. Mag. 1835, p. 161.

† Brewster called attention to similar phenomena produced by coloured outlines in 'Brit.-Assoc. Report,' 1848, p. 48, "On the Vision of Distance as given by Colour." He there gives a rather laboured explanation, comparing the vision of different distances for the differently coloured lines to the phenomena of the lenticular stereoscope. He adds that "the difference of distance of the coloured lines or spaces may be appreciated even with one eye." Compare also Helmholtz, *Physiologische Optik*, p. 645.

Compare also an experiment with a disk of black paper on a background of pale ultramarine, by Prof. O. N. Rood, 'Silliman's Journ.' xxxi. 1861, pp. 343, 344.

There is little doubt that Wheatstone's phenomenon of the "Fluttering Hearts" (see 'Brit.-Assoc. Rep.' 1844) is due to the attempt of the eye to focus for adjacent spaces of colours of unequal refrangibility, which could not, therefore, be in distinct focus at one time. The same peculiar fluttering is observed when white objects on a dark ground are observed through a purple solution of permanganate of potash.

‡ Phil. Trans. 1852, p. 4.

suggests change of distance." I think that the muscular sensation of convergence of the eyeballs serves rather to give an idea of rate of change of distance * ; and I have just indicated the cases to which variation of retinal magnitude are limited.

24. In Wheatstone's classical research of 1838 it was demonstrated how great is the capacity of the brain to combine together two slightly differing retinal images. This faculty once admitted, however explained, renders it unnecessary here to discuss how far the inexactness of focus for any particular tint is concerned in binocular vision. In the present paper it must suffice to treat of the non-achromatism of the eye in its relation chiefly to monocular vision. And, for reasons stated in § 19, we shall omit further reference to linear perspective, since its relation to our perception of distance is not based upon apparent colour, or upon the formation of an exact retinal focus.

IV. *Experimental Results, and Deductions.*

25. Fraunhofer † is generally credited with the first careful attempt to measure the chromatic aberration of the eye. His method of experiment consisted in placing a wire in the principal focus of a telescope, in which the focus was then obtained by the adjustment of the lenses of an achromatic eyepiece. The theoretical adjustment to distinct vision for the various coloured rays was then calculated and compared with the actual adjustment ; and the difference between theory and observation was assumed to measure the aberration of the eye. The method is at best only indirect ; and there appears to be some doubt whether in the critical experiments an achromatic object-glass as well as an achromatic eyepiece was employed. Nevertheless, under the conditions of the experiment, the measurements were very accurately made, and are therefore invaluable.

26. I have found the most satisfactory exhibition of chromatic aberration to be manifested when a solution of permanganate of potash was employed, in a narrow glass trough, as a medium to intercept the middle rays of the spectrum. I have also tried solutions of iodine, and cobalt glasses of various depths of tint ; but none are so satisfactory. For some experiments I have employed a piece of thin cobalt glass in conjunction with a solution of permanganate. By this means I have obtained media transmitting red and blue-

* See a curious little footnote by Mr. A. J. Ellis at p. 97 of his edition of Helmholtz's 'Sensations of Tone.'

† See Gilbert's *Annalen*, lvi. 1814, p. 304; Helmholtz, *Physiol. Optik*, p. 128; Brewster, 'Edin. Phil. Journ,' xix. p. 25.

violet rays freely, but totally opaque to all rays between D and E, and nearly opaque to rays from C to D in the orange, and from E to F in the green and blue.

27. A silvered bead placed in the sunlight, and viewed through such a medium can by no possibility be seen with accurate focus for all rays. It appears either as a near red point of light surrounded by a blue haze, or as a distant blue light surrounded by a red haze *. The point of light seems to change distance from far to near, or from near to far, with the effort of the eye. This effect, however, is only to be well observed when the intensities of the red and blue rays are about equal; for if either predominate, the eye will focus for the brighter unless special care is taken to adjust and keep the required focus.

28. The researches of Jurin, Schreiner, Müller, Powell, and Trouessart have tended in favour of the view that the eye is achromatic at least for objects at the centre of the field of vision, when distinctly in focus. The fundamental illustration of this view is as follows:—Take any visible white object—say a square inch of white paper upon a black background. If the eye be focused for a distance beyond the white surface, it will appear blurred at the edges, being tinged outwardly with orange-yellow, inwardly with blue. But if the eye be focused for a point nearer than the white surface, it will appear tinged outwardly with blue, inwardly with orange-yellow, while at exact focus these bordering tints disappear. To explain this seeming achromatism of the eye it was argued by Wollaston, Young, Müller, and Matthiesen that the rays passed almost without refraction along the axis of the eye, and therefore suffered no dispersion †. On the other hand, in my own experiments with permanganate-of-potash solution to intercept the yellow and green rays, I have never been able to obtain a luminous surface small enough to be free from aberration at the edges—which proves that the focus is really not exact. The rays of the middle of the spectrum, being more intense, mask the effects of the feebler rays; and the eye focuses for the more intense light, as I have mentioned in § 27.

29. If, on the contrary, a weak solution of picrate of potash be employed as a screen to cut off the extreme red

* This effect may be shown objectively to an entire audience by casting beams of light from a lamp through such a purple medium upon a silvered ball.

† Baden Powell contended that the refraction and dispersion of the vitreous humour being in the opposite sense to that of the crystalline lens, aqueous humour, and cornea, compensated the dispersion for axial pencils.

and violet rays, it is very difficult with *any focus* to observe the tinted margins.

30. Moreover the apparent achromatism of the experiment above mentioned is only found with pencils nearly coincident with the axis of the eye. Oblique pencils always give tinted margins in white light. This may be verified by looking at a set of concentric circles in white and black. If the eye be steadily focused for the white centre, no colours are seen at its margin, but may be observed at the inner and outer edges of the other circles. I have always found it possible to get yellow exterior margins to a white object at any distance; that is, I have always found it possible to focus for a further distance; but not *vice versâ*.

31. If a square of white paper be carefully tinted around the edge with blue, and laid on a black ground, it appears further off than a perfectly white square of the same size beside it, since the blue margin helps to correct the yellow rays that surround the image at a longer focus. In short, a blue-edged square appears like a white square looked at with too near a focus. The opposite effect is observed with a margin tinted yellow.

32. I adjusted a lenticular stereoscope to easy focus, then placed in it a sheet of white paper having two equal circles 1 centim. in diameter, described upon it at the appropriate distance—one red, the other blue. The joint effect of these two gave, apparently, a combination of a red circle with a slightly larger one of blue. On drawing a slightly smaller circle of blue, with the circle of red as before, they appeared to give exact coincidence.

33. Knowing the power of the eye to reconcile retinal images in magnitude (see § 16), I placed in the stereoscope a penny coloured blue and a halfpenny coloured red. They refused to be seen as one object. On replacing them by a red penny and a blue halfpenny, coincidence was, with some difficulty, obtained.

34. My next experiments attempted the direct estimation of the distance of objects by the focus of the eye apart from other means of estimation. A conical tube of metal, blackened interiorly, was taken, through which only a limited field of view was possible, the eye being placed at the smaller aperture. In front of this tube a screen of blackened cardboard was placed, capable of adjustment to any distance from 10 centims. to 350 centims. from the tube, and covered the entire field of view. Coloured glasses could be introduced in front of the tube. The objects displayed upon the cardboard screen in the centre of the field of vision were irregularly shaped pieces of

white paper. These were cut by an assistant and adjusted—their distance and size being unknown to the observer, and varied between each experiment. Hence, under the conditions given, the eye could form no judgment of distance based upon apparent magnitude, upon parallax, or upon apparent form or shadow; the estimation depended solely upon the muscular sensation of adjustment to focus. After a little practice this became moderately easy with white light, and the estimations were fairly within limits. With a screen of yellow glass interposed no difference was experienced. When a ruby-red glass was employed, however, the estimations were generally, though not invariably, too small, and with a cobalt-blue glass generally (though not invariably) too great. The following is the mean of six experiments taken at random from a number made with a red glass, and of another six from those made with a blue glass.

	Red.	Blue.
Mean real distance	208 centims.	178 centims.
Mean estimated distance	163·1 „	199 „

35. When a solution of permanganate was employed in conjunction with a blue glass, giving equal intensities of red and blue rays, the attempt to estimate the distance of the white pieces of paper became perplexing in the extreme. The object seemed to be moving backwards and forwards as the focus changed from red to blue and blue to red.

36. After about forty experiments with blue and red glasses, the errors became less. Evidently the effect of practice was to sophisticate the result, the mind knowing the probable result beforehand, and making allowance involuntarily. The forty experiments were not all made at one time, because the eye becomes fatigued when experimentation is prolonged; and as in my own case with fatigue partial astigmatism sets in, I was careful to test my vision from time to time, to avoid error from this source *.

37. Every book on Art will tell us that blue is a "retiring" colour, while red is an "advancing colour." For long I had

* Since the experimental results recounted in this paper have been chiefly obtained with my own eyes, it may be well to state the following particulars:—For objects in centre of field of vision there is no trace of colour-blindness; neither eye is astigmatic when not fatigued; their range of accommodation is from 11 centims. to infinity, and with good definition at all ranges; the blind-spots are distinct, the foveæ centrales well formed and sensitive; there is no difficulty in perceiving Purkinje's figures and Haidinger's brushes and lavender streaks. Let me add, as a test of definition, that on a clear night I can easily see twelve stars of the Pleiades.

been convinced that these alleged characteristics were something more than associations with blue sky and red rocks; and the universality and tenacity with which artists pronounce this opinion is surely indicative of a reality somewhere. The opinion of Goethe on this point sums up the whole matter. I quote from Sir Chas. Eastlake's edition of the 'Farbenlehre'*.

"As the upper sky and distant mountains appear blue, so a blue surface seems to retire from us."

"Rooms which are hung with pure blue appear in some degree larger, but at the same time empty and cold."

38. So the blueness of the lower misty air may, as Alpine travellers know, cause the base of a mountain actually to appear *more distant* than its summit. Mr. Ruskin has noted this in his 'Modern Painters'†; and the fact has been familiar to artists for centuries, having been described by Leonardo Da Vinci in his *Trattato della Pittura*, and is alluded to by Goethe.

39. The sun and moon when red at setting or rising, and the moon when red in total eclipse, look nearer—or, some people say, larger—than at other times.

40. For the sake of giving prominence or nearness to the foreground of a picture, painters will contrive to introduce a scarlet flower, or a patch of red rock, or a figure dressed in red—a practice sanctioned and well known in Art, but quite inexplicable except on the train of reasoning we have been attempting to follow.

41. The immense importance of these facts of physical and physiological optics has long been recognized in Art. The study of aerial perspective has been carried long since to a pitch that renders it worthy to be put upon a basis more than merely empirical. There can be little doubt that other empirical laws may be similarly accounted for. Visitors to picture-galleries may be constantly observed scanning a landscape through a rolled up catalogue, or under the arched fingers of the hand. Is there not an explanation, too, for this? The square frame of gold asserts the flatness of the surface, and prevents the mind from realizing that which the eye perceives—that all the rays of light do not focus at once upon the retina, but that each tint retires or advances to its own appropriate distance. Landscapes without figures or architecture, especially, are improved by this method of treatment; and the reason is plain: in them the eye judges the

* Goethe's 'Theory of Colours,' translated by Sir C. L. Eastlake, R.A., F.R.S. (London: 1840). p. 311. par. 780 and 783.

† Vol. i. p. 182.

scene by colour, not by retinal magnitudes or binocularly compound sensations.

42. I have endeavoured to apply the method of experimentation in another direction. Take any picture in which there are well-expressed foregrounds and distances, and look at it through the coloured media employed in the earlier experiments. If the facts of distance are expressed only indirectly, by suggestions of magnitude, by linear perspective of vanishing lines and the like, the interposition of a red or a blue glass will produce little effect, except that the latter may deaden the intensity of the shadows. If, however, the expression of distance in the picture is accomplished chiefly by aerial perspective (that is to say, by colour), a red glass will almost destroy the intelligibility of the picture, while a blue glass will draw out the distances in a marked manner.

43. Reflecting how useful is the purpose subserved thus by the non-achromatism of the eye, I consider it probable that if the eye were so constructed as to be originally achromatic, having usually blue distances and red-brown foregrounds to look at, it would, by an inevitable process of natural selection, develop into a non-achromatic instrument.

Summary and Recapitulation.

44. I would conclude therefore :—

(α) That the muscular sensation of the adjustment to focus of the lenses of the eye affords a possible means of estimating distances.

(β) That when binocular methods, and those depending on association of visible form or magnitude fail, the eye falls back on colour as a means of estimating distance.

(γ) That estimates of distance founded on apparent magnitude are liable to be rendered fallacious by the colour of the object.

(δ) That, conversely, estimates of distance founded on colour are liable to be confused by apparent magnitude.

(ϵ) That colour may in some cases outweigh, as a criterion, the evidence of binocular vision.

(ζ) That the chromatic aberration of the eye accounts for the universal opinion of painters as to the "retiring" character of blue, and the "advancing" character of red tints.

(η) That Aerial Perspective in Art is a true expression of a physical fact in the perception of distance.

University College, Bristol,
May 8, 1877.

VII. *Note on a Curious Effect of Absorption of Light.* *By* Silvanus P. Thompson *.

WHEN experimenting upon the chromatic aberration of the eye, I had occasion, as mentioned in a recent communication to the Physical Society, to employ aqueous solutions of permanganate of potash of various degrees of density as absorbing media. It is well known that solutions of this salt, when sufficiently dense, absorb all the rays of the middle portion of the spectrum, while freely transmitting red, blue, and violet rays. Desiring, for the purposes of experiment, to obtain a medium which should transmit in equal intensity the two groups of rays of greatest and least refrangibility, I found it advisable to somewhat reduce the intensity of the red rays by passing the beam of light through a thin glass plate tinted with pale cobalt. This plate was placed in front of the glass trough containing the permanganate solution. The compound medium was totally opaque to rays between lines D and E, nearly opaque to rays between C and D in the orange and between E and F in the blue.

The surfaces of objects reflecting ordinary white light, when viewed through this medium, possessed a remarkable shimmer or lustre (almost like the "stereoscopic lustre" of Dove), as if there were two surfaces both reflecting light—a red surface, and a blue surface behind it and seen through the red surface.

When a coloured tablecloth or carpet was viewed through the medium, the portions coloured yellow, orange, or red appeared all equally red, and to be standing up above the surface in a plane nearer to the eye. The other portions (those of blue or green tint) appeared all alike of a blue-violet and as if sunk to a lower plane.

On observing a landscape-painting a similar effect was produced, the blues and greys of the picture appearing of a blue-violet, while all the yellows, reds, and even the bright greens of the picture stood out, in deep-red tints, almost detached from the plane of the picture.

On turning from coloured drawings to an actual spring landscape the same startling phenomenon was repeated; for, while the sky gleamed with a steel-grey tint, the colour of the young green leaves, the sunlit grass, and the tiled house-roofs was alike *blood-red*. It was hard to resist the notion that the absorbent medium had actually changed the tint of the light; but actual comparison with the spectroscope showed that the deep red observed existed among the rays of ordinary light reflected by the objects in question.

* Communicated by the Author.

The only analogous effect that I have observed in nature was about twelve months ago, when just after a sunset the slightly hazy but cloudless eastern sky in the Thames valley near Maidenhead was of a remarkable purple hue; and I noticed that trees and grass reflecting the light from this aspect presented a most unwonted redness of tint.

VIII. *On Action at a Distance in Dielectrics.*

By S. H. Burbury*.

If K be the specific inductive capacity of a dielectric medium, V the potential of any electrified system, then, according to Professor Clerk-Maxwell (Electricity and Magnetism, vol. i. p. 86), the characteristic equations of V become, (1) at a point in the medium where the volume-density of free electricity is ρ,

$$\frac{d}{dx}\left(\mathrm{K}\frac{d\mathrm{V}}{dx}\right)+\frac{d}{dy}\left(\mathrm{K}\frac{d\mathrm{V}}{dy}\right)+\frac{d}{dz}\left(\mathrm{K}\frac{d\mathrm{V}}{dz}\right)+4\pi\rho=0; \quad . \quad (\mathrm{A})$$

(2) at an electrified surface where the surface-density is σ,

$$\mathrm{K}\left\{\frac{d\mathrm{V}}{d\nu}-\frac{d\mathrm{V}}{d\nu'}\right\}+4\pi\sigma=0; \quad . \quad . \quad . \quad . \quad (\mathrm{B})$$

in which $\frac{d\mathrm{V}}{d\nu}$ is the rate of increase of V per unit of length of the normal on the outside of the surface measured outwards, and $\frac{d\mathrm{V}}{d\nu'}$ the increase in the same direction inside the surface. Assuming the truth of these equations, it can be shown that in a heterogeneous medium the attraction exerted by an electrified particle at O on another particle at P does not act generally in the line OP, is not generally a function of the distance OP, or of circumstances existing at O and P only, or at points in OP only. It becomes, then, a matter of irresistible inference that a particle at O exerts no direct "action at a distance" on the particle at P, but acts upon it derivatively through the medium.

For, let it be required to find the force of attraction at P exerted by unit particle at O. There being no other electrified body in the field except the particle, equation (A) becomes, at all points in space,

$$\frac{d}{dx}\left(\mathrm{K}\frac{d\mathrm{V}}{dx}\right)+\frac{d}{dy}\left(\mathrm{K}\frac{d\mathrm{V}}{dy}\right)+\frac{d}{dz}\left(\mathrm{K}\frac{d\mathrm{V}}{dz}\right)=0. \quad . \quad . \quad (\mathrm{C})$$

If, now, K were constant, this would further reduce to

* Communicated by the Author.

$$\frac{d^2V}{dx^2}+\frac{d^2V}{dy^2}+\frac{d^2V}{dz^2}=0,$$

which admits of integration in the form

$$V=\frac{1}{\sqrt{x^2+y^2+z^2}}=\frac{1}{r},$$

r being the distance of the point (x, y, z) from O. Hence it follows that the attraction varies inversely as the square of the distance.

But in the general case, K being variable, equation (C) does not admit of integration, and the attraction at P cannot be found, unless from the differential equation. In order to effect this object, we will first obtain another form of equation (C), applicable to the whole of space outside any electrified system.

II. Consider the series of equipotential surfaces due to such a system, and let lines be drawn cutting them all orthogonally, so as to form a "tube of force."

Comparing the equation (C) with the equation of continuity in hydrodynamics, we see that an incompressible fluid might flow through all parts of the medium with component velocities

$$K\frac{dV}{dx},\quad K\frac{dV}{dy},\quad K\frac{dV}{dz}.$$

The direction of motion of such a fluid would evidently be at every point perpendicular to the surface V = constant through the point; that is, it would be always along the axis of our supposed tube.

Also if $d\nu$ represent an element of length of such a tube, the actual velocity of the fluid along it would be $K\frac{dV}{d\nu}$. If, then, a be a section of the tube perpendicular to the axis, we have as the condition of incompressibility, that $aK\frac{dV}{d\nu}$ is constant throughout the tube. Our equipotential surfaces must then possess this geometrical property, that $aK\frac{dV}{d\nu}$ shall be constant throughout every tube of force that can be drawn through them.

It can here be shown that the equation (C) is supported by analogy; for if, instead of a dielectric, the medium were a conductor having $\frac{1}{K}$ for resistance per unit length and unit area, then the equation $aK\frac{dV}{d\nu}=$ constant expresses Ohm's law.

III. We shall now pass to the following problem. Given a distribution of matter over a closed surface S, known to have constant potential V_0 at every point of that surface, to find all the equipotential surfaces due to that same distribution.

It may be shown, as in Thomson and Tait's 'Natural Philosophy,' Appendix A, that the potential of the given distribution, having the constant value V_0 at every point on S, has that same constant value also at every point within S. For, let V be the potential of the distribution, U any other function whatever of (x, y, z) which is equal to zero at every point on S. Then, if the triple integral refer to the whole space within S, we have

$$\iiint K\left\{\left(\frac{dV}{dx}-\frac{dU}{dx}\right)^2+\left(\frac{dV}{dy}-\frac{dU}{dy}\right)^2+\left(\frac{dV}{dz}-\frac{dU}{dz}\right)^2\right\}dx\,dy\,dz$$
$$=\iiint K\left\{\left(\frac{dV}{dx}\right)^2+\left(\frac{dV}{dy}\right)^2+\left(\frac{dV}{dz}\right)^2\right\}dx\,dy\,dz$$
$$+\iiint K\left\{\left(\frac{dU}{dx}\right)^2+\left(\frac{dU}{dy}\right)^2+\left(\frac{dU}{dz}\right)^2\right\}dx\,dy\,dz$$
$$-2\iiint\left\{\frac{dU}{dx}K\frac{dV}{dx}+\frac{dU}{dy}K\frac{dV}{dy}+\frac{dU}{dz}K\frac{dV}{dz}\right\}dx\,dy\,dz. \quad (1)$$

By Green's theorem the last line of the second member of this equation is equal to

$$-2\iint UK\frac{dV}{dv}\,ds$$
$$+2\iiint U\left\{\frac{d}{dx}\left(K\frac{dV}{dx}\right)+\frac{d}{dy}\left(K\frac{dV}{dy}\right)+\frac{d}{dz}\left(K\frac{dV}{dz}\right)\right\}dx\,dy\,dz,$$

where in the first term the double integration is extended over the whole surface S, and $\frac{dV}{dv}$ is the increase of V per unit length of the normal inside S. But the first term vanishes, because U is by hypothesis zero at every point on S; and the second term vanishes because of (C). Rejecting then the last line, equation (1) becomes

$$\iiint K\left\{\left(\frac{dV}{dx}-\frac{dU}{dx}\right)^2+\left(\frac{dV}{dy}-\frac{dU}{dy}\right)^2+\left(\frac{dV}{dz}-\frac{dU}{dz}\right)^2\right\}dx\,dy\,dz$$
$$=\iiint K\left\{\left(\frac{dV}{dx}\right)^2+\left(\frac{dV}{dy}\right)^2+\left(\frac{dV}{dz}\right)^2\right\}dx\,dy\,dz$$
$$+\iiint K\left\{\left(\frac{dU}{dx}\right)^2+\left(\frac{dU}{dy}\right)^2+\left(\frac{dU}{dz}\right)^2\right\}dx\,dy\,dz. \quad . \quad . \quad . \quad (2)$$

This equation holds true whatever U be, provided it be zero at

every point on S. We may therefore make $U = V - V_0$, which satisfies that condition, since $V = V_0$ at every point on S. In that case

$$\frac{dU}{dx} = \frac{dV}{dx}, \quad \frac{dU}{dy} = \frac{dV}{dy}, \quad \frac{dU}{dz} = \frac{dV}{dz},$$

and (2) becomes

$$2\iiint K \left\{ \left(\frac{dV}{dx}\right)^2 + \left(\frac{dV}{dy}\right)^2 + \left(\frac{dV}{dz}\right)^2 \right\} dx\,dy\,dz = 0.$$

Now K cannot be negative, and cannot be assumed always zero. The above equation, then (which, as we have seen, holds universally if V be constant over the surface S), cannot be satisfied unless

$$\frac{dV}{dx} = 0, \quad \frac{dV}{dy} = 0, \quad \frac{dV}{dz} = 0,$$

and $V = V_0$ at every point within S. It follows that $\frac{dV}{d\nu'}$ in equation (B), which is the rate of increase of V with the normal on the inside of S), must be zero. Applying, therefore, equation (B) to our surface, σ being the surface-density, and making $\frac{dV}{d\nu'}$ zero, we have

$$K \frac{dV}{d\nu} + 4\pi\sigma = 0.$$

Here, as will be remembered, $\frac{dV}{d\nu}$ is the rate of increase of V per unit of length of the normal from S outwards.

IV. Hence as K and σ are known at every point of S, $\frac{dV}{d\nu}$ is also known at every point of S, and we can therefore describe round S the equipotential surface S_1 corresponding to $V_0 - \delta V$, δV being any infinitely small increment of potential. It will be at a distance from S equal to $\frac{K}{4\pi\sigma}\delta V$.

Further, having now obtained two consecutive equipotential surfaces belonging to our distribution, the property of our surfaces investigated above, namely that $aK\frac{dV}{d\nu}$ is constant throughout every tube of force, enables us to construct all the others. For if we take as base of our tube any element of area on S, and call it a, then $aK\frac{dV}{d\nu}$ is known at the base of the tube; also if normals forming the tube be drawn from all points on the boundary of a, and if they cut out from the

second surface S_1 the area a_1, a_1 is known, depending on the curvature of S and the known distance between the surfaces.

Also K_1, the value of K on the area a_1, is supposed known. If then $\frac{dV}{dv_1}$ be the rate of increase of V per unit of length of the normal on the second surface, the relation $a_1 K_1 \frac{dV}{dv_1} = aK \frac{dV}{dv}$ determines $\frac{dV}{dv_1}$. This, again, being known at every point of the second surface enables us to describe a third equipotential surface, that, namely, corresponding to $V_0 - 2\delta V$. And so on *ad infinitum*. By this means we can describe round S a series of surfaces which satisfy with S the geometrical condition of making $aK \frac{dV}{dv}$ constant throughout every tube of force. And they are the only series of surfaces including S which can satisfy that condition ; they must therefore be the equipotential surfaces due to the distribution on S.

V. It is evident from the mode of formation of these surfaces, that if S_p be the equipotential surface passing through an external point P, the form of S_p would be altered if we altered K at any point in the space between S and S_p, and its distance from any neighbouring equipotential surface would be altered in like manner. This is equally true however small the surface S may be, and is therefore true if it be an infinitely small surface—that is, if it represent an electrified particle at O. Hence, as we undertook to show, the attraction exerted at P by a particle at O does not generally act in the line OP, is not a function of OP, or of circumstances existing at O or at P or at any points in the line OP only. It becomes then difficult, if not impossible, to conceive "action at a distance" between O and P.

VI. It might perhaps be objected that, by the supposed alteration of K anywhere between S and S_p, we should alter the potential of the distribution on S, so that it would no longer be constant at every point of S. But this, if true, involves the assertion that the potentials of particles constituting the distribution on S are dependent on the values of K at all points between S and S_p, however distant S_p may be. It follows, then, as before, that the attraction between two particles of the distribution cannot be direct action at a distance.

VII. We have shown above how, having given any distribution on S, making V constant at every point of S, to form all the other equipotential surfaces due to that distribution. The problem then suggests itself, how to ascertain whether any given distribution on S has this constant potential or not,

and hence to find the potential at any point due to a given distribution. For this purpose we may make an assumption, viz. that a distribution of uniform density over a sphere must, if that sphere be small enough and K be continuous, have uniform potential over the sphere. If this be so, the above process determines all the equipotential surfaces due to such a distribution.

But any electrified particle may be regarded as a distribution uniform in density over an infinitely small sphere. Hence the equipotential surfaces due to any electrified particle can be determined by the above process. Hence, further, the potential of any electrified system can be determined, being the sum of the potentials of its several parts. The inference that we have drawn above respecting action at a distance does not depend on this assumption respecting the potential of a particle, and remains valid whatever be the true solution of the problem of finding the attraction of a particle.

IX. *Proceedings of Learned Societies.*

ROYAL SOCIETY.

[Continued from vol. iii. p. 538.]

Feb. 22, 1877.—Dr. J. Dalton Hooker, C.B., President, in the Chair.

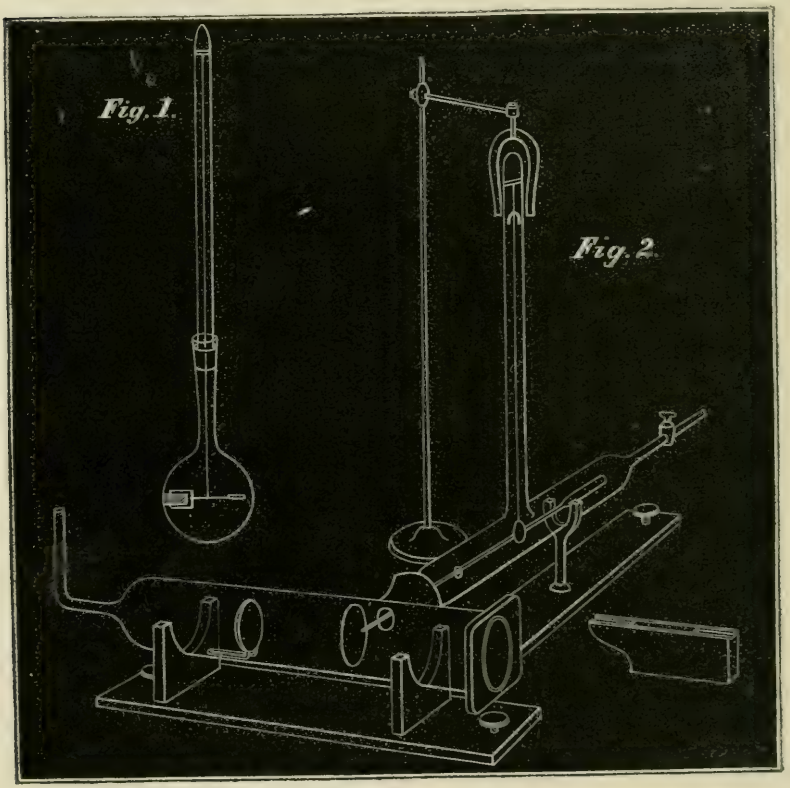
THE following paper was read:—

"On Crookes's Force." By G. Johnstone Stoney, M.A., F.R.S., and Richard J. Moss, F.C.S.

In two papers by one of the authors of the present communication, which appeared in the Philosophical Magazine for March and April 1876, it has been shown that the motion of the blackened disks of a Crookes's radiometer can be explained by the known dynamical properties of the trace of gas which is present, and the term "Crookes's force" is proposed to designate the reaction which comes into play between the blackened disks and the walls of the exhausted chamber when a difference of temperature exists between them. Shortly after the first of these papers appeared we commenced an experimental investigation of the subject with the view of learning, if possible, the laws to which the force conforms. The investigation is still in progress; and being exceedingly tedious, it will require a great expenditure of time before it is completed; we propose, however, in this preliminary paper to describe the apparatus and methods of observation employed, and to give some of the results already obtained.

If the pressure which is exerted on the blackened pith surfaces reacts on the sides of the glass envelope, it follows that a transparent disk delicately suspended close to a stationary disk of

blackened pith ought to move away from the pith, and therefore towards the light, when the pith is illuminated. This inference was submitted to the test of experiment by means of an apparatus represented in fig. 1 and constructed as follows:—A piece of elder-pith 2·5 centims. in length and 1·2 centim. in breadth, blackened on one side, was fastened by one end to the interior surface of the bulb of an ordinary boiling-flask (of about 200 cub. centims. capacity) in such a manner that the free end of the pith extended towards the middle of the bulb. A light glass rod with a small magnet on one end, and a disk of thin microscope-glass on the



other end, was so suspended in the bulb that the glass disk could be readily balanced in a position nearly parallel with the surface of the blackened pith, and a few millims. distant from it. The silk fibre from which the glass rod was suspended hung from a fixed arm at the upper end of a tube, the lower end of which was hermetically fastened into the neck of the flask. An elongation of this tube (not shown in the figure) with a contraction for sealing, served to connect the apparatus with the exhaust-tube of a

Sprengel pump. The pump was set in action, and occasionally the flame of an ordinary gas-burner was held at a distance of about 10 centims. from the blackened pith while the microscope-glass was closely watched. When the gauge of the pump showed a tension of 7 millims., as compared with the mercurial column of a barometer standing in the same vessel of mercury, the glass disk was distinctly repelled from the pith and towards the source of light. As the exhaustion was continued the repulsion between the pith and the glass increased. The apparatus was sealed off from the pump when the mercury falling in the exhaust-tube had for some days produced a metallic sound. Feeble illumination now caused the glass disk to be forcibly driven away from the pith*.

We now endeavoured to determine quantitatively the influence of variations in the tension of the residual gas, and also the influence of variations in distance between the reacting surfaces. For this purpose we constructed the apparatus represented in fig. 2.

On a wooden stand supported by three levelling-screws rests a glass tube 20 centims. in length and 3·8 centims. in diameter, having a tubular opening at one side, into which is cemented horizontally a smaller tube 1·5 centim. in diameter. In the larger tube there is a circular disk of elder-pith 2·3 centims. in diameter, having one side blackened with lampblack; it is supported in a vertical position on a movable stand of iron wire. By means of a magnet the pith disk can be moved up and down the tube, and thus placed at any required distance (within 12 centims.) from a delicately suspended circular disk of thin microscope-glass, 3 centims. in diameter and 0·3 millim. in thickness. The glass disk is attached to the end of a glass arm, which is suspended in the smaller tube by means of a silk cocoon fibre contained in a vertical limb 38 centims. in length and 9 millims. in diameter. In order that the torsion of the silk fibre may be conveniently regulated, there is a small ∩-shaped piece of iron wire attached to it a few centimetres below the end from which it hangs. A horseshoe magnet is suspended outside the tube with the piece of wire between its poles. By turning the magnet round, torsion may be imparted to the silk fibre. The balance of the glass arm is adjusted by means of a small iron ring which it carries; the position of the ring can be altered at will by an external magnet. There is a small silvered mirror attached to the arm at the point of suspension; this reflects the image of a narrow illuminated slit onto a scale divided into degrees 2·5 millims. each. An alteration in the position of the index amounting to 0·5 millim. is readily observed; this corresponds with a change in the position of the outer edge of the glass disk amounting to 0·033 millim. One end of the large tube is ground perfectly flat, and closed by cementing to it a plate

* The apparatus was sealed off on the 14th of April, 1876. The experiments described above were made in March.

of glass 4 millims. in thickness; through this light is admitted to the pith disk by an arrangement to be presently referred to. The other end of the large tube is contracted and terminates in a narrow tube bent upwards, partly packed with gold leaf (to intercept mercury vapour), and attached to the exhaust-tube of a Sprengel pump. The smaller tube terminates in a contraction bearing a stopcock which serves for admitting the gases to be experimented upon.

We found it necessary to avoid the irregular actions which arose when the incident light was allowed to shine on the inside of the glass tube. This was accomplished by projecting on the disk the image of a uniformly illuminated circular aperture in a screen of copper foil placed outside the glass chimney of an Argand gas-burner. The lens employed for this purpose is permanently attached to a stand on which the lamp is secured. When the position of the pith disk is altered, the position of the stand carrying the lamp and lens is altered to the same extent; so that the pith disk is always in focus. The burner is automatically supplied with coal-gas at the uniform rate of 3·2 cubic feet per hour, this being the quantity that gives a flame of the required size.

We found that the torsion of a cocoon fibre furnishes a force which is too variable to admit of its being delicately controlled by the method just referred to; but a very accurate adjustment was secured by a supplementary arrangement. It has already been mentioned that the arm which bears the thin glass disk carries a small iron weight by which its balance is regulated. This weight was made to serve for balancing the torsion of the silk fibre. For this purpose a small bar magnet sliding in a groove is so placed that one pole acts on the weight. With a little care the distance of the magnet from the weight can be adjusted so as to bring the index to zero, and thus exactly counterbalance the torsion of the silk, the index remaining practically stationary. In this condition the apparatus is sensitive to an extreme degree.

It will be observed that in this apparatus the cooler of the heat-engine consists of the swinging disk along with that part of the containing tube which lies between the swinging disk and the disk of blackened pith. By thus making a portion of the cooler freely movable, we hoped to be able to ascertain the thickness of the layer of gas within which Crookes's force exists. It would not have answered for this part of our investigation to have made the heater the part freely movable (as in all apparatus of the kind that had been previously constructed), because the heater cannot be placed far from the cooler in apparatus that is not inconveniently large for the Sprengel pump, since when the containing tube is of any moderate size its sides become the principal part of the cooler* when the glass disk is at a distance.

* It is obvious, from the dynamical theory, that if the molecules tending in one direction within a stationary gas are at one temperature, while the rest

With the improved apparatus repulsion at first appeared to exist at all tensions in hydrogen, the distance between the disks being 1 millim. This repulsion was not perceptibly increased by alterations in tension, until the latter was reduced to about 200 millims., when a slight increase of repulsion took place; and further reductions of tensions were in each case followed by an increase of repulsion.

It was observed that when repulsion was detected at ordinary tensions the glass disk occupied the upper portion of the containing tube, and that, when the disk was made to swing in the lower portion of the tube, instead of being repelled it was attracted towards the pith when illuminated. These results are obviously due to convection-currents. By carefully balancing the glass disk as nearly as possible in the centre of the tube the effects are greatly reduced; but it would be very difficult, if not impossible, to balance the disk in a perfectly neutral position.

In an atmosphere of hydrogen at ordinary atmospheric tensions there is no indication of attraction or repulsion when the distance between the pith and glass disks is 100 millims. and the time of illumination 15 seconds, a period which experience has led us to adopt. The first unmistakable indications of pressure on the swinging disk at this distance occur when the tension is about 50 millims., at which tension there is a very feeble repulsion. As the tension is reduced the repulsion increases. An extensive series of experiments have been made for the purpose of determining the ratio in which the repulsion increases for given reductions in the tension of the residual gas. The accompanying Table exhibits the results of one set of experiments:—

T = tension of the residual gas.
D = distance between the disks in millims.
P = pressure on the swinging disk, as represented by the space, in degrees of the scale, through which the index passes in 15 seconds.

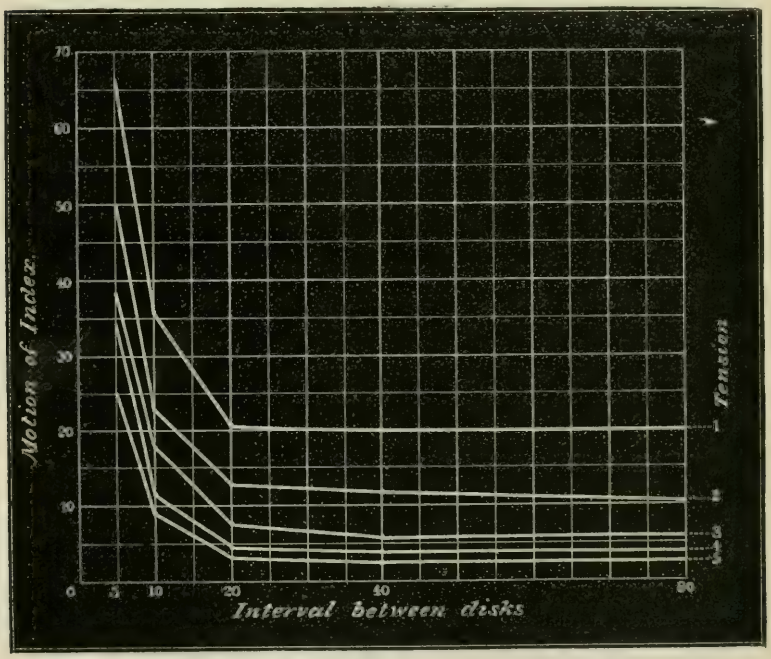
of the molecules of the gas and the surface of a solid with which they come into contact are at another temperature, then the Crookes's force which arises may be either normal to that surface like the pressure of a gas, or tangential to it like friction, or in any way compounded of these two, being in each case in the direction spoken of above.

Accordingly the forces that act upon the containing vessel and the vanes of radiometers are in general partly tangential and partly normal; so that in estimating the intensity of these forces the matters to be considered, along with the directions of the motions in the intervening gas, are the proximity and extent of the opposed surfaces, and not the degree of their parallelism. It is probable that all the phenomena of radiometers with crumpled or inclined vanes, which Mr. Crookes has lately investigated, admit of explanation by these considerations.

It is manifest that in the apparatus described in the text the chief part of the reaction on the containing vessel, when the disks are at a considerable distance asunder, consists of tangential forces acting on the inside of the tube.

T.	D.	P.
50	100	$\frac{1}{4}$ c
20	,,	$\frac{1}{2}$
10	,,	$1\frac{1}{8}$
5	,,	$2\frac{1}{2}$
4	,,	3
3	,,	4
2	,,	5
1	,,	$8\frac{1}{2}$

In the above experiments it will be observed that the distance between the pith disk and the swinging glass disk was constant, viz. 100 millims. We have made several series of experiments, with the disks at various distances, in atmospheres of various tensions. The means of several of these series are graphically represented in the following diagram. The ordinates represent the distance in millimetres through which the index moved in a period of 15 seconds; the abscissas represent the distance in millimetres between the disks.



Our expectation of being able to ascertain the thickness of the Crookes's layer has not been entirely fulfilled with the apparatus as at present constructed, owing to the presence of the exceedingly feeble force that is represented by the horizontal portions of the diagram. We have found this feeble force nearly constant at

each tension when the two disks are at any distances asunder exceeding 20 millims. So far as we have been able to ascertain, it seems to arise partly from the sudden expansion of the gas throughout the extent of the Crookes's layer as soon as the light is turned on (an expansion which acts on the swinging disk as if a feeble explosion had taken place in front of it), and partly from a Crookes's force acting between the upperside of the tube and the swinging disk (caused by the inside of the tube becoming sensibly heated by the convection-current that commences as soon as the Crookes's layer is established). We do not think that any appreciable part of it is due to the *direct* action of the convection-current.

The rest of the diagram represents the forces which we found when the disks were at distances of 10 and 5 millims. asunder. The forces which presented themselves at these distances are to be attributed mainly to a true Crookes's reaction between the disks; and they seem to warrant the conclusion that Crookes's reaction was manifested at a distance of at least 10 millims. in a hydrogen vacuum, when the outstanding tension was as much as 5 millims. of mercury.

At distances of from 20 to 80 millims. the very feeble force acting on the glass disk in our apparatus seemed to vary about inversely as the tension. As already mentioned, it appeared to be nearly independent of the distance when the distance exceeded 20 millims.

At distances of 5, 10, and 20 millims. the force on the swinging disk made some approach to varying at each tension inversely as the distance. But, so far as may be judged from our measures of such exceedingly feeble forces, there is a sensible deviation from this law at most of the tensions.

Moreover the diagram, taken as a whole, seems to suggest, in conformity with the dynamical theory, that the law changes with variations of density; for if the law were the same at all the observed tensions, the converging lines in the diagram should converge to points in the axis of abscissas, whereas they converge towards points lower down.

We will postpone the further discussion of the observations already made with this apparatus until we can supplement them by others.

GEOLOGICAL SOCIETY.

[Continued from vol. iii. p. 541.]

May 9th, 1877.—Prof. P. Martin Duncan, M.B., F.R.S., President, in the Chair.

The following papers were read:—

1. "On the Agassizian genera *Amblypterus*, *Palæoniscus*, *Gyrolepis*, and *Pygopterus*." By Ramsay H. Traquair, Esq., M.D., F.R.S.E., F.G.S.

2. "On the Circinate Vernation, Fructification, and Varieties of *Sphenopteris affinis*, and on *Staphylopteris? Peachii*, Etheridge and

Balfour, a genus of Plants new to British Rocks." By C. W. Peach, Esq., A.L.S.

3. "On the Occurrence of a Macrurous Decapod (*Anthrapalæmon Woodwardi*, sp. nov.) in the Red Sandstone, or Lowest Group of the Carboniferous Formation in the South-East of Scotland." By Robert Etheridge, Esq., jun., F.G.S.

4. "On the Stratigraphical Position of the Corals of the Lias of the Midland and Western Counties of England and of South Wales." By R. F. Tomes, Esq.

May 23, 1877.—Prof. P. Martin Duncan, M.B., F.R.S., President, in the Chair.

The following communications were read:—

1. "Remarks on the Coal-bearing Deposits near Erekli, the ancient Heraclea Pontica, Bithynia." By Rear-Admiral T. A. B. Spratt, C.B., F.R.S., F.G.S.

In this paper the author described the occurrence of true Coal-measures near Erekli, on the north coast of Asia Minor, from observations made by him when on service in the Black Sea in 1854. The coal was obtained near Kosloo, about 30 miles east of Erekli, where it cropped out on the sides of a valley, and was worked by horizontal drifts. The district was much disturbed by faults, and the workings could only be driven from 100 to 400 yards into the hill. In the eastern ridge bounding the valley of Kosloo there were 11 or 12 seams of coal of different thicknesses in a distance from N. to S. of about 2 miles, one of them being about 18 feet thick, and the best coal forming a seam of 4 ft. 10 in. The seams dipped S.E. about 26°. They were interstratified with shales, sandstones, and conglomerates of quartz-pebbles, and occasionally with thin bands of clay and ironstone. From some of the seams the author obtained fossil remains of plants, which sufficiently prove that these coals belong to the Carboniferous period. They include, according to Mr. Etheridge, species of *Lepidodendron*, *Lepidostrobus*, *Calamites*, *Pecopteris*, *Sphenopteris*, *Neuropteris* (?), *Sigillaria*, *Stigmaria*, *Glossopteris* (?), and *Sphenophyllum*. The author also noticed several other localities in the immediate neighbourhood where coal was known to exist under somewhat similar conditions. He also referred to the geology of Erekli itself, and noticed especially the occurrence of patches of more or less altered shales and marls, probably of middle Tertiary age, overlying the igneous rocks of which the country consists.

2. "On the Structure and Affinities of the genus *Siphonia*." By W. J. Sollas, Esq., B.A., F.G.S.

3. "On the Serpentine and associated Rocks of the Lizard District." By Rev. T. G. Bonney, M.A., F.G.S., Fellow and late Tutor of St. John's College, Cambridge.

The author stated that considerable doubt appeared still to exist as to the true relations of the Lizard serpentine and the associated hornblende schists, and as to the origin of the serpentine. He had carefully examined all the junctions accessible on the Cornish coast;

inland they are generally obscured. Some of them are concealed by débris, &c.; but the majority prove beyond doubt that the serpentine is intrusive. Further, almost everywhere large fragments of hornblende schist are caught up and included in the serpentine.

Besides the serpentine there is a large mass of gabbro at Crousa Down, and many dykes and veins along the east coast almost to the extremity of the serpentine region. At Coverack Cove, near the above mass, are gabbros of two ages, the older much resembling a kind of troktolite; on microscopic examination it proves to be chiefly plagioclase felspar, augitic minerals (including diallage), and olivine partially converted into serpentine; there is a red and a green variety. The newer, a coarser gabbro, appears to be of the same age as the other veins on the coast, and connected with the main mass. Some remarkable changes have taken place in this also. In certain places it exhibits a separation of its mineral constituents, causing it to resemble a foliated rock. This is proved to be due to pressure at right angles to the structure. The minerals also are often changed. The felspar is replaced by a white granular mineral resembling saussurite; the diallage (which occurs sometimes in very large crystals) is often partially, or even wholly, converted into rather minute crystalline hornblende. In these specimens there is no olivine to be distinguished. The great mass, however, is rich in olivine; yet a weathered specimen from it, resembling in aspect the gabbro of the veins, does not show olivine. Hence the author believes that in certain cases the olivine, instead of being converted into serpentine, aids in forming the hornblende. Further, there are dykes and veins over the same area of a dark trap. Some of these are augitic, others hornblendic. The author believes that, at any rate in certain of these, the hornblende is of secondary formation. On the west coast are veins of granite; those on the east coast, said to be granite, prove, on careful examination, to be altered rock, remarkably like granite veins, but not really such.

In discussing the origin of the serpentine, the author called attention to a structure commonly seen, which appeared to be a true "fluidal structure." He then described the result of microscopic examination of many specimens of the Lizard and some other serpentines. Commencing with slightly altered Lherzolite (from the Ariége), he traced the change through the older gabbro of Coverack to the serpentine rock of that place, which contains a large quantity of unaltered olivine, and so to other serpentines in which the olivine is quite replaced by the mineral serpentine. He described also the mode of the change. The other minerals found in the serpentine rock are enstatite, varieties of augite, and occasionally a fair quantity of picotite, with, of course, oxides of iron. Hence he concluded that, as had been already shown as regards some other serpentines, that of the Lizard was the result of the hydrous alteration of an olivine rock, such as Lherzolite.

4. "On certain ancient Devitrified Pitchstones and Perlites from the Lower Silurian District of Shropshire." By S. Allport, Esq., F.G.S.

In this paper the author described a series of ancient vitreous and

semivitreous lavas, with their associated agglomerates and ashes, constituting the ridge of Ercal Hill, Lawrence Hill, and the Wrekin, and the low ridge parallel to this to the west, both of which are marked as "greenstone" on the Geological-Survey Map. Their composition and structure show them to have been originally identical with some of the glassy volcanic rocks ejected during the most recent geological periods. After noticing the geological relations of these rocks, the author described the structure of modern perlitic and spherulitic rocks, and pointed out that the spheroidal balls which characterize them are produced by a process of more or less concentric cracking during the contraction of the mass after it has been solidified. He then indicated the characters of the ancient rocks of the Lower Silurian district of Shropshire, and showed their identity of structure with the modern spherulitic pitchstones and perlites; he also noticed that in some instances they had become devitrified. As the result of his investigation, he says that the structure of these rocks proves their original vitreous condition, for the perlitic and spherulitic formations, with their associated microliths, are only observed in connexion with the obsidian or pitchstone varieties of volcanic glass—and that in the older as in the younger series there is the same gradation between the vitreous and stony varieties.

June 6th, 1877.—Prof. P. Martin Duncan, M.B., F.R.S., President, in the Chair.

The following communications were read:—

1. "On the Rank and Affinities in the Reptilian Class of the *Mosasauridæ*, Gervais." By Prof. R. Owen, C.B., F.R.S., F.G.S.

2. "Note on the Occurrence of the Remains of *Hyænarctos* in the Red Crag of Suffolk." By Prof. William Henry Flower, F.R.S., F.G.S.

3. "On the Remains of *Hypsodon*, *Portheus*, and *Ichthyodectes* from British Cretaceous strata, with descriptions of new species." By E. Tulley Newton, Esq., F.G.S., of H.M. Geological Survey.

4. "On the Precarboniferous Rocks of Charnwood Forest." Part I. By the Rev. E. Hill, M.A., F.G.S., and the Rev. T. G. Bonney, M.A., F.G.S.

The authors described a mass of slates, grits, and volcanic breccias, accompanied by some knolls and dykes of syenite, spread over a space of about 50 square miles. They showed that the patches marked on the Survey Map as Greenstone of Bardon, Birchwood, and Buck Hill, except a very small portion of the latter, are really altered rock, that the Syenite knoll of Bawdon Castle carries a mass of breccia in its centre, and that the area of the Syenite in Bradgate-House Woods must be enlarged.

Several writers have noticed that part of the porphyritic region of the north-west corner is altered rock. The authors showed that there is in it no igneous rock at all, and that the same is the case with every one of the smaller patches marked as porphyry on the Survey Map. All are volcanic breccias, ashes, or agglomerates,

some of enormous size. The extent to which volcanic materials enter into the rocks of the district is remarkable.

The authors endeavoured to correlate the stratified rocks, and adduced evidence to prove that the pebble and ash beds of Forest Gate, the grit and pebble beds of the Hanging Rocks, the similar beds in the grounds of A. Ellis, Esq., at Swithland, and the quartzites of Bradgate-Stable Quarry, Groby Pool, and Steward's-Hay Spring form one horizon, the slate breccias of Blores Hill, Bradgate, Ulverscroft Mill, Markfield, Bardon, and High Towers a second, the coarse ash-beds of Benscliff, Chitterman Hill, Timberwood Hill, and the Monastery a third, and the quartzose rocks of Charley Wood, Charley, the Old Reservoir, and Blackbrook a fourth.

Hence they showed that the beds are considerably dislocated near the syenites, which removes the main objection which previous writers have urged against these being intrusive; and they described the evidence they have obtained as to this being their real nature. This evidence included the description of actual contacts of igneous and sedimentary rock seen at two points in the wood south of Bradgate House, and at a third in Bradgate Park.

They propose, in a continuation of the paper, to touch upon the faults, and to describe in greater detail the microscopic structure of the rocks.

X. *Intelligence and Miscellaneous Articles.*

ON THE EQUILIBRIUM OF PRESSURE IN GASES.

To the Editors of the Philosophical Magazine and Journal.

GENTLEMEN,

THERE is one point in connexion with my paper "on the Mode of the Propagation of Sound"*, published in the last Number of your Journal, on which I would say a few words. As regards the *process* whereby the molecules of a gas automatically adjust their motions so as to move equally towards all directions, and thus produce equilibrium of pressure, it should be stated, to prevent any possible misconception, that this depends (as deduced by Professor Maxwell) on the oblique collisions of the molecules causing an equal flow of *vis viva* towards all directions, thus producing equilibrium of pressure in all directions.

The *fact* that the molecules of a gas move equally towards all directions (so that an equal number of molecules are moving in any two opposite directions) was deduced by me from the observed fact of the equilibrium of pressure; but this deduction is not original, inasmuch as the same fact had been previously deduced, without my knowledge, by Professor Maxwell.

I am, Gentlemen,

Yours faithfully,

London, June 8, 1877. S. TOLVER PRESTON.

* "Mode of the Propagation of Sound, and the Physical Condition Determining its Velocity, on the Basis of the Kinetic Theory of Gases," Philosophical Magazine, June 1877.

ON A DIRECT TRANSFORMATION OF MECHANICAL WORK INTO ELECTRICITY. BY E. GUIGNET.

In most physical institutions we find *electrical motors* (Froment's system more or less modified). The École Polytechnique of Rio de Janeiro possesses such a motor formed of five fixed electromagnets and a movable barrel furnished with six bars of soft iron. The current of ten Bunsen elements being thrown into the wire of the electromagnets, the barrel turns briskly from right to left, or from left to right, according to the general direction of the current. Moreover a commutator, carried by the axis, changes the direction of the current, in each of the electromagnets, at every fifth part of a revolution.

This apparatus has for a long time served for showing how an electric current, whatever its origin, can produce work, doubtless very costly, but of which the expense depends directly upon the net cost of the current. The same apparatus can be used for the inverse demonstration—a fact which appears to me important for the instructor; for the experiment is easily carried out in any lecture-room.

If the two extremities of the wire of the electromagnets be put in communication with any galvanometer (which need not be very sensitive), turning with the hand the barrel of the motor will be sufficient to establish the formation of a continuous current whose direction changes with that of the rotation. It can even be proved thus that the intensity of the current increases with the velocity of rotation, at least up to a certain limit.

Finally, the same experiment makes evident *induction under the influence of the earth*. Several contrivances have been devised to render this curious phenomenon sensible—notably the ingenious hoop of M. Delezenne. In the foregoing experiment the soft-iron bars become magnetized under the influence of the earth. Their changes of position with respect to the fixed electromagnets give rise in the wires to induction-currents which are gathered into a single current by the commutators. Therefore the maximum effect will be obtained when the axis of the barrel is parallel to the inclination-needle; but, on account of the charge on the cushions, it is better to place the apparatus so that the axis is horizontal and parallel to the declination-needle.

It is likewise easy to show that the magnetization of the soft-iron bars and of the electromagnets increases with the velocity of the rotation. When the barrel turns very slowly, the two soft irons scarcely attract iron filings, in consequence of the earth's magnetism; but as the operation proceeds, when the velocity reaches several rotations per second, the soft irons can lift large quantities of iron filings.

On replacing the bars of soft iron of the Froment motor by electromagnets wound round with a wire communicating with that of the fixed electromagnets, a genuine dynamoelectrical machine would be obtained, of the class of the Gramme machines without permanent magnets; but the performance of such a machine would

doubtless be very mediocre, especially on account of the sparks given by the commutators. We constantly employ here, as a source of electricity, an excellent Gramme machine moved by steam-power. This machine consumes only one horse-power, and produces a light equal to 100 Carcel burners, quite sufficient for all lecture-experiments.—*Comptes Rendus de l'Académie des Sciences*, May 14, 1877, tome lxxxiv. pp. 1084, 1085.

ON THE DISTRIBUTION OF TEMPERATURE IN THE CONDUCTING-WIRE OF A GALVANIC CURRENT. BY HEINRICH STREINTZ.

If a galvanic current is led through a wire, the temperature of the wire rises until the stationary condition enters—until, namely, in every corporeal element of the wire exactly as much heat is excited as is carried off through the surrounding particles to the surface and through this into the environing medium.

Leaving out of consideration the ends of the wire, the calculation is a problem of the plane. If k denotes the conducting-power for heat, u the temperature at any point of the cross section, the expression

$$k\left(\frac{d^2u}{dx^2}+\frac{d^2u}{dy^2}\right)dx\,dy\,dt$$

represents the amount by which the heat brought to a surface-element from the circumjacent elements exceeds that which is carried away.

According to Joule's law, the quantity excited during the same time by the galvanic current is

$$wi^2\,dx\,dy\,dt.$$

For the stationary state the sum of the two expressions must be equal to nil; hence

$$\frac{du^2}{dx^2}+\frac{d^2u}{dy^2}+\mathrm{J}=0;\quad \mathrm{J}=\frac{wi^2}{k}.$$

As integral of the equation, we obtain

$$u=\mathrm{A}-\frac{\mathrm{J}}{4}r^2+\mathrm{B}\log nr.$$

Since, for obvious physical reasons, B must be $=0$, only A remains to be determined. Given the surface-temperature τ of the wire, and calling its radius a, then

$$u=\tau+\frac{\mathrm{J}}{4}(a^2-r^2). \quad \ldots\ldots\ldots\ldots\ldots \quad (\mathrm{I.})$$

But if for τ the coefficient of the *external* heat-conducting power H be substituted, the condition-equation

$$\left(\frac{du}{dr}\right)_{r=a}+h(u-\mathrm{U})_{r=a}=0,\quad h=\frac{\mathrm{H}}{k},$$

is added, in which U denotes the temperature of the surrounding medium, and we obtain

$$u=\mathrm{U}+\frac{\mathrm{J}}{2h}a+\frac{\mathrm{J}}{4}(a^2-r^2). \quad \ldots\ldots\ldots\ldots \quad (\mathrm{II.})$$

For the numerical calculation, h and J must be known. But J, originally expressed by resistance, current-intensity, and conducting-power, can also be expressed by h and the surface-temperature attained; for from the comparison of equations I. and II. it follows that

$$J = \frac{2h}{a}(\tau - U).$$

I determined h by experiment thus: through a thick-walled brass tube I caused hot water of a known temperature to flow, and observed the temperature on the outer surface of the mantle. Theory gives for this case

$$h = \frac{\tau_2 - \tau_1}{c_1(\tau_1 - U)(\log \text{nat}\, c_1 - \log \text{nat}\, c_2)},$$

in which τ_1 and τ_2 denote the temperatures, c_1 and c_2 the radii, of the outer and inner circumferences; and then the result of the observations is

$$h = 0{\cdot}00078.$$

For a brass wire it can now be calculated how much the temperature at the centre is higher than that at the surface; and when $a = 0{\cdot}25$ millim., $\tau = 55°{\cdot}5$ C., $U = 18°$ C., we get

$$u_c - \tau = 0°{\cdot}0037 \text{ C.}$$

Without making further observations, the temperature-difference can now be calculated for other wires also.

In conclusion, I must not omit to mention that Edlund, in the May Number of Poggendorff's *Annalen*, has also given a calculation of the distribution of temperature in a galvanically heated wire; his deduction, however, proceeds quite differently from that here given; the equations obtained are not so general, and the numerical data are based on experiments of another kind than those I have employed; so that I had no hesitation in making public my investigations, which were ready before the appearance of Edlund's memoir.—*Auszug aus dem am* 12. *Aug.* 1876 *der Redaction von Pogg. Ann. d. Phys. u. Chemie eingesandten Manuscripte.*

ON THE SPECIFIC HEATS OF GASES.

To the Editors of the Philosophical Magazine and Journal.

Gentlemen,

Mr. Burbury has pointed out to me a mistake in my paper on dissociation in the June number of the Philosophical Magazine which is important. On page 415, the sign of I should be changed. This will affect the ratio of the specific heats given on p. 417; in the first case $\frac{c'}{c}$ will be 1·585 instead of 1·609, and in the second 1·338 instead of 1·423. Consequently the reasoning at the end of § 20, which depends on these ratios, will be invalidated. If the quantity I were positive, as in the paper, we should get gases cooling when they combine, or passing from one state into a less stable state.

I am, Gentlemen,

Yours truly,

W. M. Hicks.

THE

LONDON, EDINBURGH, AND DUBLIN

PHILOSOPHICAL MAGAZINE

AND

JOURNAL OF SCIENCE.

[FIFTH SERIES.]

AUGUST 1877.

XI. *On Chemical Classification.* *By* M. M. Pattison Muir, *F.R.S.E., Assistant Lecturer on Chemistry, The Owens College, Manchester* *.

1. "BY the classification of any series of objects is meant the actual or ideal arrangement together of those which are like and the separation of those which are unlike, the purpose of this arrangement being, primarily, to disclose the correlations or laws of union of properties or circumstances, and, secondarily, to facilitate the operations of the mind in clearly conceiving and retaining in the memory the characters of the objects in question."†.

In the classification of a series of objects we wish to discover the deepest and most general resemblances which hold good between these objects; we do not wish for mere arbitrary definitions. In a perfect system of classification, each class of objects must be distinguished from all other classes by some quality or qualities admitting of accurate definition; these qualities, or at least one of them, must be of comparatively easy recognition; and, further, these properties must be really correlated with every member of the class; that is, each and every property must exist in each individual of the class.

The advantages of such a classification are apparent. Given a new object, by inspection or experiment we discover that this object possesses one of the more marked characteristics of a certain class; we therefore infer that it possesses the remaining characteristics of this class: hence we at once learn a great

* Communicated by the Author.

† W. Stanley Jevons, modifying the words of Huxley, 'Principles of Science,' vol. ii. p. 348.

deal concerning the new object. The difficulties of such a classification are also apparent. We may find certain properties correlated together in two individuals; these individuals we form into a class. Yet we may discover another individual having properties which almost oblige us to admit it into this class, and nevertheless in one or more of its properties it shall differ from the 100 individuals originally examined. For instances, the metals formed a tolerably well-defined class of substances before the time of Davy. One of the apparently best established characteristics of this class was high specific gravity; this mark was correlated in all the known metals with malleability, lustre, a certain position in the electric series, &c. But Davy discovered two substances which were possessed of specific gravities less than that of water, but which the chemist was nevertheless obliged to admit into the class of metals.

The mark, *the* characteristic of a class, is not therefore always that property which strikes the casual observer as in a high degree diagnostic of the class.

There is another allied source of difficulty in classification: although we have examined with the greatest care the individual objects forming a class, and have established the universal correlation of certain properties, it is nevertheless possible that new substances may be discovered which shall exhibit the whole of these properties save one. We shall probably be obliged to admit the new substances to the class which we have formed; but we shall at the same time be obliged to define anew the properties of the members of the class. Of course it would be possible to make a new class for the newly discovered substances; but if the general analogies of these substances point to a close connexion between them and the members of the class already established, the formation of a new group, for the sake of maintaining unchanged the old definition, would be equivalent to doing away with one of the chief advantages of a rational system of classification.

2. It appears, therefore, as if every system of classfication of natural objects and phenomena must of necessity be subject to frequent, and sometimes to radical alterations. Each scheme of classification is a more or less perfect representation of the state of knowledge in that branch of science to which it applies at the time of its production.

With the advance of knowledge the scheme of classification must change. Moreover there must be minor and subsidiary systems of classification underlying the wider and more general scheme. To take an instance from chemistry: the modern system of classification is mainly founded on the valency of

the elements ; but the arrangement of the elements into groups according to their valency does not interfere with the arrangement of the same elements into other groups in accordance with their specific gravity, their electric and thermal conductivity, their malleability, their atomic weights, &c. &c. In fact, the nearer we rise to a perfect system of classification (which, however, we can never attain to) the more useful do the subsidiary schemes of classification become. We begin even now to see some connexion between the grouping of the elements in accordance with their atomic weights, and the grouping in accordance with general physical properties, or with valency.

3. In an actual system of classification as practised in any branch of science we find a more or less complete fulfilment of the requisites of a perfect system. The qualities by which each class is marked off from all other classes of objects sometimes admit of very accurate definition, sometimes they are more vague. Each and every property regarded as characteristic is not always existent in every member of the class.

In cases where it becomes very difficult to define the essential characteristics of a class, recourse is sometimes had to classification by types. An ideal type is erected, to which the members of a given class more or less approximate. This method of classification has been used to a considerable extent in the biological sciences. "The type of each genus should be that species in which the characters of its group are best exhibited and most evenly balanced"*.

A similar method has been adopted in chemistry. Perplexed with the difficulty of giving such a definition of the term "metal" as should mark off one group of elementary bodies from that other group the members of which are commonly known as metalloids, chemists have endeavoured to imagine a substance possessing certain well-marked properties, some of which are always exhibited by those elements which by common consent are designated as metals. According as any element in its general properties approaches to or recedes from this ideal type, so is it to be classed among the metals or among the non-metals. Such a scheme of classification is evidently most incomplete, and is altogether wanting in those characteristics which are the marks of a perfect system. In how far must the individual element approach the type in order that it shall be admitted to the class of metals? Must an element aspiring to be called a metal possess three fourths of those properties which are characteristic of the type, or will the half be considered sufficient? A scheme

* Waterhouse, quoted by Woodward in 'Rudimentary Treatise of Recent and Fossil Shells,' p. 61.

of classification by types leads, if logically carried out, to the establishment of a number of subsidiary classes, each characterized by its own qualities.

4. The various systems of classification which have predominated in chemical science may be broadly divided into two groups :—those in which chemical substances have been classified in accordance with the functions performed by them ; and those in which chemical substances have been classified in accordance with their composition. I shall endeavour to give a slight historical sketch of the various systems of chemical classification.

5. Before the time of Black, Cavendish, Priestley, and Lavoisier and his associates, we find chemists paying almost exclusive attention to the action of bodies without inquiring into their composition. We find accounts of many experiments upon the mutua action of salts and acids, metals and semimetals, and so on ; but, because of the absence of measurements of the quantities of the various reacting bodies, we find nothing but vagueness. The mere qualitative study of reactions never led to any far-reaching generalizations.

Casual coincidences, vague analogies, were followed up ; principles were imagined to exist in various substances ; and by the supposed existence of these imagined principles substances were grouped together. Thus we have the principle of acidity, the mercurial principle existent in metals, and many other similar fantasies.

The nomenclature of chemistry at the time preceding that of the introduction of Bergman's system was a nomenclature based in many particulars on the mere qualitative study of reactions. Such names as *oil of vitriol*, *butter of antimony*, *liver of sulphur*, *sugar of lead*, *milk of lime*, &c. call attention only to the outer and shallow analogies of appearance, consistence, colour, &c. of the substances named. According as attention was directed to this or to that reaction of one and the same substance, so was a different name devised for that substance ; thus we meet with carbonate of potassium under the names of *fixed salt of tartar*, *fixed vegetable alkali*, *chalky tartar*, *alkahest of Van Helmont*, &c. &c.

The study of qualitative reactions could lead to no true conception of the essential function exerted by any substance ; hence not only in the nomenclature, but also in actual practice do we find constant failure to distinguish between essentially distinct substances. The fact that a substance effervesced on addition of acid appears to have been adopted as characteristic, and to have led to the confused grouping together of several different compounds under the name of Alkali. But

with the appearance of Black's famous research upon the mild and caustic alkalies, a new era in chemical classification takes its beginning. The use of quantitative experiment introduced by Black was vigorously pursued by Cavendish, Lavoisier, and the French chemists; and soon the method began to bear fruit.

6. Lavoisier's 'Elements of Chemistry,' when compared with such a work as Macquer's 'Chemistry,' published some thirty years before, appears to deal with an entirely new science; or, rather, the latter book has scarcely any claim to be regarded as a scientific treatise, while the former possesses the requisites of such a work in a marked degree. The honour which is everywhere paid to the name of Lavoisier is due to him, it appears to me, not so much because of any discovery of what happens when a body burns, as because of the new method which he was the first to carry out systematically in chemical research and in chemical classification. Lavoisier endeavoured to throw aside preconceived notions concerning natural objects, and to rise to true generalizations by reasoning from actually observed facts. His definition of an element is still regarded as the only truly scientific definition which can be adopted*.

From a study of the products obtained by burning phosphorus, carbon, sulphur, &c. in oxygen, Lavoisier was led to regard all acids as substances rich in oxygen. Further, partly from his definition of an element, partly from the study of the substances just mentioned, he was led to regard every salt as formed by the union of an acid with a radicle, the radicle itself being either simple or compound. This conception of the composition of salts found its full development in the dualistic theory of Berzelius.

But Lavoisier could not follow out his own method with perfect exactitude. He was still so far under the trammels of the school which preceded him, as to be unable to escape alto-

* Lavoisier's words are as follows (Ker's translation of Lavoisier's 'Elements of Chemistry,' Preface, p. 22):—"If by the term Elements we mean to express the simple and indivisible atoms of which matter is composed, it is extremely probable we know nothing at all about them; but if we apply the term *elements* or *principles of bodies* to express our idea of the last point which analysis is capable of reaching, we must admit as elements all the substances into which we are able to reduce bodies by decomposition. Not that we are entitled to affirm that those substances which we consider as simple may not themselves be compounded of two or even of a greater number, of more simple principles; but since these principles cannot be separated, or, rather, since we have not hitherto discovered the means of separating them, they act with regard to us as simple substances; and we ought never to suppose them compounded until experiment and observation have proved them to be so."

gether from the sway of imagined "principles." Although he knew of oxygen only in the form of gas, he nevertheless could scarcely accept the results of experiment, but endeavoured to regard gaseous oxygen as pure or "concrete" oxygen, *plus* a something which he called *caloric*. He appears to have thought that all "pure" substances were solids, and that by combining with this subtle kind of matter, caloric, they became first liquids and then gases. In Lavoisier's time the conception of matter and force as distinct, but real, existences had not become generally accepted among scientific men, although the *Principia* had been written sixty years before. The doctrine of Phlogiston, although extinguished in its more palpable form by Lavoisier himself, keeps, nevertheless, reappearing in this theory of the action of caloric. If we interpret both theories, the Phlogistic and the Caloric, in the light of modern doctrines of energy, we find much truth in each. Again, Lavoisier's generalization regarding the nature of acids was not based upon a sufficiently large number of facts. This generalization led him astray; it led him to forsake the plan of strictly experimental inquiry which he had laid down for himself. On the hypothesis that all acids contain oxygen, it followed that muriatic acid must contain this body; but no one had been able to separate oxygen from muriatic acid; hence, on Lavoisier's own showing, he should not, on the strength of a few experiments and a sweeping generalization, have regarded this acid as a compound of oxygen with an unknown radicle. Again, although he found that certain elementary substances were oxidized by heating with oxide of manganese or with oxide of mercury, he was nevertheless not justified, judged in the light of his own method, in assuming that the action of the former of these compounds upon muriatic acid was an oxidizing action, and in therefore concluding that the gaseous product of this action was a more highly oxygenated body than muriatic acid itself. An appeal to facts and an interpretation of the observed facts in accordance with the true scientific method which he had laid down, would have prevented Lavoisier from perplexing the chemical world with his "unknown radicle of muriatic acid" and with his "oxygenated muriatic acid." But when we see the errors which are being constantly made in our interpretation of facts, even when we receive that aid which the advance of science affords to modern naturalists, we cannot be otherwise than astonished at the small number of mistakes made by Lavoisier, nor can we grudge him the highest praise for the wonderful use which he made of his great powers of scientific imagination.

If pushing feeble analogies too far led Lavoisier astray as regards the constitution of hydrochloric acid and chlorine, a somewhat similar use of analogy led him to true ideas regarding the constitution of the alkaline earths.

Lavoisier observed that metals dissolved in acids with effervescence, and that bases dissolved without effervescence ; he further observed that lime and magnesia dissolved in acids without effervescence : hence he inferred that the latter substances are probably compound bodies. In this case Lavoisier put forward his views regarding the constitution of these alkaline earths in the form of an hypothesis only ; the hypothesis was useful as a guide in future work, and was most fruitful of good results. In the cases of hydrochloric acid and of chlorine, Lavoisier put forward what was really an hypothesis, founded on much the same kind of evidence as the hypothesis concerning the nature of lime and magnesia, as an ascertained fact. The false fact retarded the advance of science, and raised many prejudices in the minds of chemists which future investigators found it hard to remove.

7. The views of Lavoisier concerning the constitution of salts were developed by Berzelius in the terms of his famous theory of Dualism.

Starting with the assumption that a salt is formed by the union of an acid with a simple or compound radicle, Berzelius represented all salts as built up of two parts held together by electric force of some kind. These two parts might consist of two simple elements, or of two radicles themselves built up of almost any conceivable number of elements. However complicated the radicles, Berzelius regarded the salt as consisting of two distinct parts tied together, as it were, by an electric cord, which was sometimes assisted by the intervention of a third radicle called a copula. The rise of the atomic theory furnished Berzelius with a means for presenting his hypothesis in its most favourable colours. The idea that chemical union is a union between atoms seemed to find its natural outcome in the theory of Berzelius. If atoms combine, why cannot groups of atoms do the same? Can we avoid regarding a salt as made up of bundles of atoms, these bundles being themselves composed of simpler atoms? The theory of Dualism appeared to explain the composition of all known compounds ; it was triumphant.

If we compare the views of Berzelius with those of the predecessors of Lavoisier, we find that while with them function was all, with Berzelius composition was supreme. The alchemists and iatrochemists asked, What does this substance do? Berzelius asked, Of what is this substance com-

posed? The futile attempts of the alchemist to found a science naturally led those who were the authors of the true chemistry to disparage the method of their predecessors to an extreme degree. Nothing was to be hoped for from a desultory gathering together of innumerable reactions; the quantitative study of the composition of substances appeared to promise brilliant results: hence Lavoisier tended to overlook the quantitative study of reactions, while paying all regard to the quantitative study of the composition of bodies. This disregard of reactions was carried to its extreme by Berzelius and his school, and found its full development in a theory which was always ready, with its compound radicles and its copulæ, to give the correct constitutional formula for each new substance as soon as it was discovered, without waiting for the tedious detail of reactions and decompositions, which, if not in keeping with the theoretically deduced formula, were to be regarded as the products of a disordered brain*.

But it was impossible that a true classification could be based upon such one-sided views as those of Berzelius and the upholders of the dualistic school. They had done their work in advancing the knowledge of the empirical composition of compounds, in determining with accuracy the combining-numbers of many elements, in insisting upon the aid to be derived from a knowledge of the composition of substances in forming a system of classification, and perhaps in paving the way for the subsequent conception of compound radicles.

8. The experiments of Dumas upon acetic and chloracetic acids mark the rise of the modern school of chemistry and of the modern systems of classification.

Dumas found that chlorine reacts upon acetic acid to form a substance possessed of many of the properties of the original acid, but nevertheless containing chlorine. The dualistic school interpreted the results of the analyses of acetic and chloracetic acids as pointing to entirely different constitutional formulæ for these bodies. If this be so, replied Dumas, whence comes the extreme similarity of properties? We have in this reasoning of Dumas a distinct partial return to the older ideas of the predecessors of Lavoisier. Function again begins to assume importance in classificatory schemes.

Dumas, Laurent, Gerhardt, and their followers founded the new school of Substitutionists as opposed to the upholders of Dualism. The new school regarded the chemical molecule as one whole, parts of which might be sometimes withdrawn and their place taken by other parts without disturbing the stability of the building. Hence the idea of com-

* See Laurent, 'Chemical Method,' Cavendish-Society Ed., p. 32 &c.

pound radicles as imagined by the school of Berzelius was exceedingly distasteful to the substitutionists. The properties of a compound depended, in their view, not so much upon the elements which it contained as upon the position of these elements.

We have in the idea of substitution, as a guide in classification, a distinct advance upon the idea of dualism. The sole point upon which the attention must be concentrated is not, says the upholder of substitution, the composition of a substance; we must also pay regard to its reactions, whether of formation or of decomposition. The new school therefore attempted to combine the older method of the study of reactions with the newer method of the study of composition; only it made the former study of real importance by giving it a quantitative significance.

At first the substitutionists were too eager, too inclined to regard position of the component elements as all important. Elated with the success which had attended their attacks upon the clumsy and often contradictory formulæ of dualism, they for a moment forgot the truths which dualism typified. Especially did they oppose themselves in opposing the conception of compound radicles. But they wanted many new facts before a satisfactory theory could be established. Destructive criticism could be carried on with the aid of but few facts; the construction of a new wide-spreading generalization was only to be hoped for as the result of long-continued and exact labour.

9. The facts which the upholders of substitution gathered together, taken along with those already amassed by their predecessors, soon obliged the adherents of the new school to look on the nature of the substituting element or radicle as influencing the nature of the compound. Thus, by substituting potassium in place of part of the hydrogen of water a strongly alkaline substance was produced; by substituting the group NO_2 for the same hydrogen, a strong acid was formed. The two products differed widely in their properties; nevertheless they might be both regarded as derived from the same original substance by substitution. Such experiments as this led to the idea of substituting radicles, which was again developed into the modern doctrine of compound radicles,—to the idea of types, which subsequently found its fullest expression in the general theory of valency,—and, lastly, to the reconcilement of the two ideas formerly opposed—namely, that all depends upon the *position*, and that all depends upon the *nature*, of the elements or radicles in a compound body.

Let us for a moment trace the development of these ideas.

Reactions were observed which could be best explained by supposing that a group of elements had moved from one compound into another without the members of the group becoming separated from one another, and without disturbing the equilibrium of the molecule of the compound into which the group entered. These groups might, or might not, be isolated; the theory did not demand any proof of their actual existence in the free state; they were regarded merely as hypothetical existences which served to bring out analogies between groups of reactions which could not find an explanation in terms of any other theory.

The application of this theory of substituting radicles was soon attended with the discovery of relationships between bodies which appeared to have but slight analogies with one another when viewed in the light of the older theory of Dualism. The researches of Liebig and Wöhler upon the benzoyl compounds found their interpretation in the theory of substituting radicles. Berzelius had also spoken of radicles: he had indeed represented all compounds as built up of radicles, simple or compound; but the radicles of dualism had almost nothing in common with those of the new school. Although the substitutionist had once denied the existence of compound radicles, he was now obliged to use these radicles as corner stones in building up the edifice of the new chemistry. But, in place of regarding the compound as consisting of two separate existences held together by a mysterious force, aided, it might be, by a third separate existence interposed between the other two, the substitutionist looked upon the molecule of a compound as essentially a whole; only he was prepared to acknowledge a structure of some kind, he would not deny the existence of parts in this whole, and he was even ready to admit that the various parts were probably grouped around a central mass to which he gave the name of compound radicle. The followers of Dumas, Laurent, and Gerhardt did not appeal, as the upholder of dualism was ready to do, to the electrolysis of salts, and claim that the separation of the salt into two or more parts (themselves compounded of simple elements) was proof of the existence of these parts in the original salt. He was aware that this method of proof could be turned against the man who employed it, and that a dozen different constitutional formulæ could be assigned to the same substance according to the reaction which was for the moment contemplated. He was content to group together the general analogies of classes of compounds, and, without insisting upon the necessary truth of his views, to endeavour to explain these re-

actions by assigning to each substance such a hypothetical structure as should include in itself the widest possible generalization.

And, proceeding thus, the upholder of the unitary system soon began to see that compounds might be distributed into certain classes, at the head of each of which might be placed one compound as typical of all the members of the class. Many substances might be derived from water by direct or by indirect substitution ; what more natural than to regard these substances as constituted on the water type? So arose the types of hydrogen, water, ammonia, and marsh-gas.

But if the genetic relations between compounds were expressed by the use of types, it was still true that vast differences in actual properties existed between many of those substances which were classed under the same type. Hence the chemist who employed types was obliged to admit that the nature of the substituting element or radicle powerfully influenced the nature of the compound produced, although the change might not be carried so far as actually to destroy the equilibrium of the system.

Thus we see how the new chemistry borrowed some of its ideas from the old—how, although at first it appeared as the destroyer of the system of Berzelius, it was eventually seen to be founded upon the truths which had underlain the dualistic theory, and was really the development of so much as was lasting in the generalizations which had preceded it.

10. But the theory of types was incomplete : it was absorbed in that of valency or atomicity.

If one half of the hydrogen in water could be replaced by a certain radicle, while another radicle was capable of replacing the whole of the hydrogen in that compound, it was natural to regard the latter radicle as in a certain sense equivalent to, or capable of doing as much work as, two of the former. So, if one third, two thirds, or the whole of the hydrogen in ammonia was replaceable by one, two, or three atoms of certain radicles, while other radicles could replace the hydrogen only as a whole, it was no far-fetched idea to regard the latter radicles as equivalent to three of the former.

Having got hold of the idea of varying equivalencies, chemists recalled the old experiments of Wenzel and Richter upon the saturation of bases by acids, in which it had been shown that different weights of such bases as lime, potash, or soda were required in order to saturate equal quantities of the same acid. These experiments led also to the idea of varying equivalents. And if it were justifiable to view compound radicles as possessed of different capacities of saturation, surely the same

idea might be extended to the elements themselves. The hydrogen in water was capable of replacement in halves, not only by compound radicles but also by elementary substances. Two derivatives of water, in which the hydrogen was partially or entirely replaced by potassium, could be prepared. Other elements, again, were capable of replacing at once the whole of the hydrogen. But one derivative of water was known in which the hydrogen was replaced by calcium; but in this derivative the whole of the hydrogen was replaced by the metal. Hence arose the idea of varying capacities of saturation of the elements—that is, of varying valencies.

It would be out of place in such a paper as the present to trace the course of the development of the idea of valency. By the discovery of the glycols, of the alcoholic nature of glycerin, of the relations existing between polybasic acids, polyacid bases, and polyatomic alcohols, the idea gradually advanced to maturity. Today valency is one of the fundamental ideas upon which the scheme of chemical classification rests.

11. I have thus endeavoured to show that the methods of classification adopted during the earlier stages of the development of chemical science may be classed as methods based upon (1) the reactions, and (2) the composition of the substances classified. I have also attempted briefly to indicate how the fusion of these two methods into a wider system, which should pay regard alike to function and to composition in attempting to frame an exhaustive classification of chemical substances, was accomplished.

In the first paragraph of the present paper I indicated the leading features of a perfect system of classification—viz. the use of qualities capable of accurate definition as means for distinguishing between class and class, the need of employing qualities some of which at least should be capable of ready recognition, and the necessity for the existence of each and every distinguishing property in each individual of a class.

Tried by these tests, each system of classification which we have briefly noticed must be pronounced wanting. The predecessors of Lavoisier were generally totally unable to define the characteristic qualities of a class. Lavoisier himself gave a sure and satisfactory definition of elementary and compound bodies; but he made much of the composition of salts; and to the question what is a salt? the chemist can hardly yet give a satisfactory answer. Berzelius viewed all compounds as dual bodies; but how are we to define the characteristics of that vast array of radicles by the combination of which all compounds were supposed to be produced? What definite knowledge did the school of dualism afford as to the correlation of

general chemical properties with the composition of the compound radicle? It required the genius of a Berzelius to pierce the veil which shrouded the inner constitution of bodies from the vulgar gaze, and to tell authoritatively, by the juxtaposition of what radicles the substance was built up. The upholders of substitution and of the unitary theory endeavoured to correlate together general chemical function and atomic structure: and in so doing they made a step in advance; for they took a wider view of the necessities of a perfect scheme of chemical classification. But general chemical function is a somewhat vague term; and the use of types as a means of classification, although doubtless a distinct gain to chemical science, almost for the time increased the vagueness. I have already pointed out some of the essential weaknesses of a classification by types: these weaknesses were illustrated in the case of chemistry. From the vagueness of a typical classification we may be said to have now emerged into the greater definiteness of a system largely based upon the valency of the elementary atoms. But does this system give us a means for definitely settling the characteristics of each class? Does it enable us to mark off class from class? Can we by its aid correlate the leading characteristics of each class with the valency of the elementary atoms? And, lastly, is there a clear connexion between valency and those chemico-physical properties of elements and compounds which modern chemistry has brought, and is every day bringing, into so great a prominence? I shall endeavour shortly to answer some of these questions.

12. But we cannot fairly regard the idea of valency as a basis for classification apart from those other ideas to which it has given rise, notably the idea of atom-linking or molecular structure. Let us therefore shortly review the more important ideas connected with this term valency*.

And at the outset it is well to bear in mind that the valency of an element is a pure number; it is the number obtained by dividing the atomic weight by the equivalent of the element. The determination of the valency of an element therefore presupposes the determination of the atomic weight and of the equivalent of that element. Those weights of different elements are said to be equivalent which are capable of binding to themselves equal weights of a third substance, immediately, and without the intervention of another body. Hydrogen is the unit of equivalency. We know of certain elements which combine immediately with hydrogen in the proportion of one atom to one

* In preparing this part of my paper I have made free use of that great work on theoretical chemistry, *Die modernen Theorien der Chemie*, by Lothar Meyer.

atom, and in this proportion only. These elements may therefore be employed, in place of hydrogen, in determining equivalents. We know also of certain compound radicles which combine immediately with hydrogen, or with those elements alluded to in the preceding sentence, only in the proportion of one atom to one atom*; we may therefore employ these compound radicles in determining equivalents. The amount of an element which combines immediately with one atom of hydrogen, or with one atom of chlorine, bromine, iodine, fluorine, methyl, ethyl, &c. is therefore the equivalent of that element. The determination of equivalents evidently supposes that the atomic weights of the standard elements are known, also that the number of atoms, in the compound under consideration, of the standard element, and also of that element whose equivalent is sought for, can be determined. Before the equivalent of an element can be known, the molecular weights of a number of compounds and the atomic weights of the elements in these compounds must be determined. Many difficulties have to be encountered in determining molecular and atomic weights. But until a number of these weights have been determined, we cannot satisfactorily deduce the equivalent of an element, and consequently we cannot fix the valency of the element.

13. The molecular weights of those compounds which are capable of passing into the gaseous state, at attainable temperatures, without undergoing decomposition, can alone be determined with accuracy in the present state of our knowledge†. Hence, if determinations of molecular weights must precede a knowledge of the valency of an element, it follows that we have as yet no accurate knowledge of the valency of a majority of the elements. Indeed, strictly speaking, we do not know with absolute accuracy the valency of any element, because, although we have determined the molecular weights of the haloid compounds, or of the hydrides, methides, &c. of many elements, we have not determined (with our present knowledge we cannot determine) the atomic weights of the constituent elements. We certainly have fixed on numbers representing the maximum atomic weights; but whether these are the true atomic weights or not we cannot say. In most cases the probability that the ac-

* Although it is scarcely correct to speak of an atom of a compound, yet in the case of certain compound radicles the expression is perhaps admissible: thus CH_3 may be regarded as the atom, $(CH_3)_2$ as the molecule of methyl.

† The method for determining the molecular weights of gaseous compounds is itself founded, like scientific methods generally, on an hypothesis; this hypothesis has hitherto fulfilled all the requisites of a good hypothesis.

cepted numbers are the true atomic weights is very great; it never, however, amounts to certainty. But in all our measurements we can only deal with greater or lesser degrees of probability, and with probability we must be content. The commonly accepted formula for potassium chloride is KCl, the atomic weight of chlorine is almost certainly 35·37, the atomic weight of potassium is very probably 39·13; but the kind of evidence upon which we base the assumption that the molecular weight of potassium chloride is represented by the formula KCl would lead us to the formula CH as expressive of the molecular weight of benzene. Conclusions as to valency drawn from a consideration of compounds whose molecular weights are unknown (that is, from compounds the densities of whose vapours have not been determined) are more or less misleading.

14. The second difficulty which must be overcome before the valency of an element can be known is the determination of the atomic weight of that element. The maximum atomic weight is best determined by estimating the smallest relative quantity of the given element contained in two volumes of any of its gaseous compounds, the usual units being employed. Here, again, we are obliged to deal only with gaseous compounds. Failing this method, or as a check upon the determinations made by this method, we have the methods of specific heat and isomorphism, and, lastly (at present most indeterminate of all), the method of general chemical analogies. Although the first method is undoubtedly the best, it may in certain cases be advisable to adopt the result obtained by methods 2, 3, and 4 in preference to that obtained by method 1. The commonly accepted atomic weight of iron is a case in point.

15. Besides these two main difficulties, viz. determinations of molecular and atomic weights, there are other subsidiary difficulties attending the estimation of the valency of an element. Chief among these stand the difficulties arising from the existence of so-called "unsaturated compounds" and of so-called "molecular compounds."

16. Compounds are known in which the whole of the "equivalents" or "combining-powers" of one of the constituent atoms are not saturated. Thus, although the great mass of evidence obliges us to regard nitrogen as a triad, or more probably as a pentad, and oxygen as a dyad element, the compound NO certainly exists. In this compound one at least of the "combining-powers" of nitrogen must remain unsaturated. So also the compound CO is an unsaturated compound, inasmuch as we must regard the carbon atom as tetravalent. These unsaturated compounds usually combine, with tolerable ease, with additional atoms: CO readily forms $COCl_2$ &c.

But it is not always easy to tell when we are dealing with unsaturated compounds. We have many reasons for believing that the compounds of the members of the nitrogen group which contain three atoms of monad radicle united with one atom of the given element are really unsaturated compounds—that the members of this group are really pentavalent. The formation of saturated or unsaturated compounds will depend largely on the total force exercised by the combining atoms; and this will be again conditioned by the circumstances under which combination takes place; so that the mere fact that a compound shows no readiness to take up additional atoms is not a certain proof that the compound is really saturated. It is only from a study of the general characters of the combining atoms, and of the analogies of the compound, that (as I shall endeavour to point out in the sequel) probable conclusions can be deduced as to the state of saturation of a compound. Conclusions as to valency drawn from the consideration of unsaturated compounds will naturally be misleading.

17. There are certain compounds, to all appearance definite chemical bodies, which are incapable of becoming gases without undergoing decomposition. Sal ammoniac, for instance, when heated, splits up into ammonia and hydrochloric acid; but when the mixed gases are allowed to cool, sal ammoniac is re-formed. Compounds which are thus dissociated by heat have been called by Kekulé and others *molecular* compounds, in contradistinction to those *atomic* compounds which are stable in the state of gases. If the structure of those compounds which are thus decomposed by heat is essentially different in kind from that of those which are stable at high temperatures, it will of course be impossible at present to make use of the former in attempts to solve the general question of valency. Apart altogether from any opinion as to the existence of "molecular" compounds, the mere fact that certain bodies are broken up when heated, and therefore cannot be obtained as gases, at once shuts out such substances from the category of those compounds which are to be taken into account when attempting to deduce the valency of an element. But inasmuch as many chemists still appear inclined to press solid and liquid compounds into their service when considering valency, and as it appears to me that the errors which are thus certain to be made (in the present state of our knowledge) can be rendered very apparent by considering the question of "molecular compounds" in general, I shall endeavour briefly to describe the two main views which have been advanced concerning these bodies, and to recapitulate shortly a few of the points in favour of each.

Very striking examples of the class of compounds under consideration are met with in the combinations of certain of the nitrogen group of elements. Sal ammoniac is one of the most common of these compounds. If this body be really a chemical compound of the composition expressed by the formula NH_4Cl, then nitrogen is a pentad element. But if this be so, why does NH_4Cl split up, on heating, into $NH_3 + HCl$? Because, answers one school of chemists, although nitrogen is a pentad, yet its "affinities" or "combining-powers" are of unequal values; three are stronger than the other two. Or the answer may be stated in a slightly altered form: The nitrogen atom is capable of exerting force in five directions; but the *amount* of force exerted is not the same for each direction. Another school gives an answer somewhat different from this. They say that the combining-powers of nitrogen are all, originally, of equal value, but that, after three of these have been saturated, the introduction of the new atoms has so modified the conditions as to cause the remaining combining-powers to be weaker than they originally were. These two answers, although differing somewhat, are yet at one in regarding sal ammoniac as a compound the same in kind as water, or hydrochloric acid, or any other body which is known to exist undecomposed in the state of gas. But a third school of chemists answers the question, Why does sal ammoniac split up when heated? in a totally different manner:—It splits up so readily because it is of an essentially different structure from those compounds which, when caused to become gases, remain undecomposed: nitrogen is really a triad; ammonia (NH_3) is a saturated molecule; Cl_2 is also a saturated molecule; but these two molecules are capable of exerting upon each other a certain degree of attraction whereby they are held together, presenting the semblance of one compound molecule, NH_4Cl, which is, however, really two molecules. Now the first view, viz. that which regards nitrogen as a pentad element and sal ammoniac as a true atomic compound, certainly allows us to explain the general analogies of the ammonium salts more readily than the other theory, which regards the nitrogen atom as trivalent. If the latter hypothesis be correct, then ammonium sulphate must be a molecular compound of NH_3 and H_2SO_4 ($=(NH_3)_2H_2SO_4$). But the analogies between this salt and potassium or sodium sulphate are many and well marked. We can scarcely, however, regard potassium sulphate as other than a salt of sulphuric acid—that is, a body in which the hydrogen of the acid is really replaced by the metallic atom potassium ($=K_2SO_4$).

But although the first view of the composition of sal ammoniac has this and many other points in its favour, which I can-

not discuss here, it does not follow that we are justified in regarding nitrogen as a pentad, and in quoting the probability of NH_4Cl, and not NH_3HCl, being the true formula of sal ammoniac, as strong evidence in favour of the assertion—because if we allow arguments as to the valency of nitrogen to be drawn from the supposed composition of sal ammoniac, there seems nothing to hinder our extending the argument so as to include such bodies as those to which the empirical formulæ NH_4ICl_4, $N_2H_6PtCl_2$, $N_2H_8PtCl_6$, $N_2H_8HgCl_4$, &c. are assigned; and if we admit these compounds, and others like them, we may make nitrogen of almost any valency we choose. We may also extend the same kind of reasoning to other elements:—Because $KClO_3$ and KNO_3 are isomorphous and show other points of analogy, chlorine is a triad or it may be a pentad; but $KClO_4$ and $KMnO_4$ are also isomorphous; chlorine appears to be a dyad or a tetrad; and so on. These and other similar contradictory results may be obtained by admitting solid bodies (that is, bodies which are either decomposed before passing into the gaseous state, or which have never yet been volatilized) as evidence in arguments concerning valency.

That such discrepancies would be found might almost be deduced *à priori* from what we know of the nature of solids, liquids, and gases. Whether we accept or reject the molecular theory of matter, we cannot but admit that there is generally a greater simplicity in the structure of gases, as indicated by their properties, than in that of liquids and solids. Two simple generalizations express, with very considerable exactitude, the action of heat and of pressure respectively upon the volumes of gases; how complicated is the expression which is required to indicate the relation between the volume of a single solid or liquid body, and increase or decrease of temperature or pressure! How shall we hope ever to frame a general expression which shall include these relations for all solids or for all liquids?

It must be admitted that the molecule NH_4Cl does not exist in the gaseous state under any conditions hitherto realized. Admitting that a substance which is a true atomic compound of N, H, and Cl in the proportion expressed by the formula NH_4Cl does exist in the solid state, we should *à priori* expect that its molecular structure would be much more complicated than this, NH_4Cl; but if it is more complicated than this, all arguments as to the valency of nitrogen which are based on the assumption that this is the true molecular formula are valueless.

But if we cannot admit, in default of further proof, the ex-

istence of a molecule NH_4Cl, must we agree with those who look on sal ammoniac as a "molecular" compound of ammonia and hydrochloric acid? I do not think that it is necessary for us to do so.

The difficulties which must be overcome by the theory of molecular compounds are numerous. First of all there is the great difficulty of defining the expression "molecular compound." How is a compound of this class to be distinguished from an atomic compound? I do not think I am wrong in saying that no one has as yet given a satisfactory answer to this question. Is the mere fact that a compound is dissociated by heat sufficient to prove that the structure of the compound is different in kind from that of stable bodies? Many substances which are dissociated by heat are nevertheless possessed of well-marked chemical and physical properties which are not the mean of the properties of their constituents. It is difficult to believe that the force holding the parts of these bodies together is essentially different from that which acts between the parts of other bodies perhaps only differing from the first in that they are capable of existing as gases. It may be, however, that in so-called "atomic" and "molecular" compounds we have the initial and final members of a series of bodies gradually passing into one another by almost insensible degrees. Even assuming this difficulty to be overcome, there remains the fact many gaseous (that is, by hypothesis, atomic) compounds are decomposed at high temperatures. Water is resolved into its atoms by the action of great heat. Where are we to draw the line and say, all substances stable immediately above this point, although decomposed at considerably higher temperatures, are atomic compounds, but all substances decomposed below this point are only molecular compounds? What are we to say to such substances as methylic and ethylic sulphates? $(C_2H_5)_2SO_4$ cannot be obtained as a gas without suffering decomposition, $(CH_3)_2SO_4$ is stable in the gaseous state.

Although we may not agree with the theory of molecular compounds, there is yet one lesson which it teaches and which we should surely be ready to learn—namely, that in all discussions as to the valency of any element we can draw safe conclusions only from a consideration of those compounds which are capable of existing in the state of gases.

[To be continued.]

XII. *A New Automatic Motion for the Spectroscope.* *By* Walter Baily *.

[Plate I.]

In this paper I propose to describe a new mechanism for moving the prisms of the spectroscope, a model of which was exhibited in the Loan Collection of Scientific Apparatus, No. 157 *a*.

The instrument is founded on the following proposition :— If a series of curves whose equations are

$$r=\mathrm{F}\left(\frac{\theta}{1}\right),\quad r=\mathrm{F}\left(\frac{\theta}{2}\right),\ldots r=\mathrm{F}\left(\frac{\theta}{n-1}\right),$$

be described on each of two disks, and one disk be turned over on the other so that the origins coincide, and the initial lines are inclined at an angle ϕ, the curves will intersect in pairs (viz. the curve $\left\{r=\mathrm{F}\left(\frac{\theta}{m}\right)\right\}$ of one disk with the curve $\left\{r=\mathrm{F}\left(\frac{\theta}{n-m}\right)\right\}$ of the other disk) at points lying on lines from the origin which divide the angle ϕ into n equal angles. For if θ be the angle measured from the initial line of one of the disks, we have at an intersection $\frac{\theta}{m}=\frac{\phi-\theta}{n-m}$; whence $\theta=m\frac{\phi}{n}$, and the series of values of θ is

$$\frac{\phi}{n},\quad 2\frac{\phi}{n},\ldots(n-1)\frac{\phi}{n},$$

and therefore the angle ϕ is divided into n equal angles. All these intersections are equidistant from the origin ; for

$$r=\mathrm{F}\left(\frac{\theta}{m}\right)=\mathrm{F}\left(\frac{1}{m}.m\frac{\phi}{n}\right)=\mathrm{F}\left(\frac{\phi}{n}\right).$$

Putting $m=0$, we have the intersection of $\left\{r=\mathrm{F}\left(\frac{\theta}{0}\right)\right\}$, which is the initial line of one disk, with the curve $\left\{r=\mathrm{F}\left(\frac{\theta}{n}\right)\right\}$ of the other disk ; here also $r=\mathrm{F}\left(\frac{\phi}{n}\right)$.

In fig. 1, K is the common origin, through which passes an axle perpendicular to the disks. One disk is fixed, and K O is its initial line ; and A A′, B B′, C C′, D D′ are slits

* Communicated by the Author, having been read before the Priestley Club, Leeds.

Fig. 1.

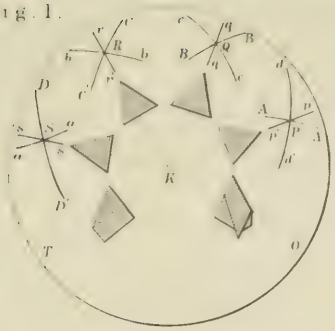


Fig. 2.

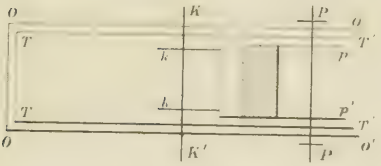


Fig. 3.

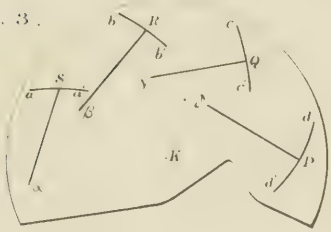
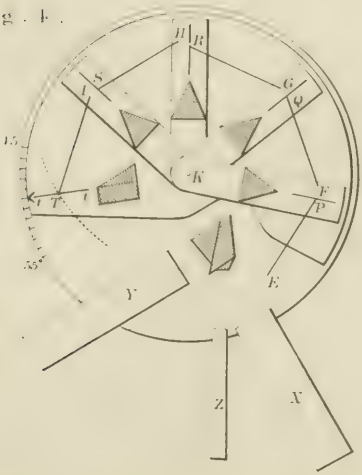


Fig. 4.



in this disk having for their middle lines the curves

$$r=\mathrm{F}\left(\frac{\theta}{1}\right),\quad r=\mathrm{F}\left(\frac{\theta}{2}\right),\quad r=\mathrm{F}\left(\frac{\theta}{3}\right),\quad r=\mathrm{F}\left(\frac{\theta}{4}\right)$$

between the same limits of r. The other disk can turn on the axle K; its initial line is K T; and $a\,a'$, $b\,b'$, $c\,c'$, $d\,d'$ are slits similar to A A′, B B′, C C′, D D′. K P, K Q, K R, K S are arms capable of turning on the axle K; and $p\,p'$, $q\,q'$, $r\,r'$, $s\,s'$ are slits in these arms directed towards K.

Now let P, Q, R, S be the intersections of the slits in the disks, and let the arms be turned so that their slits pass over the points P, Q, R, S. Then, if pins are inserted in the slits at these points, perpendicularly to the disks, the arms will be retained in such positions that the lines K P, K Q, K R, K S will divide the angle between K O, K T into five equal angles. The first prism is placed on the line K O and fastened to the fixed disk; the next four are placed on the lines K P, K Q, K R, K S and are fastened to the corresponding arms; and the last prism (half of which is replaced by a reflecting prism) is placed on the line K T and fastened to the moving disk. All the prisms are placed at the same distance from the centre; and it is obvious that they will have the motion required for the spectroscope, the angle between the position of consecutive prisms being always $\frac{\phi}{5}$.

In order to keep the pins perpendicular to the disks, I have a pair of fixed and a pair of moving disks, the slits in each pair being exactly parallel, and the moving disks being rigidly connected together; each arm also consists of two parallel arms rigidly connected. The arrangement is shown in a section of the instrument given in fig. 2. O O′ are the fixed disks, T T′ the moving disks, K K′ the axle, $k\,p\,k'\,p'$ an arm carrying one of the prisms (which is shaded), P P′ one of the pins going through the arm and all the four disks. The pins are prevented from dropping out by nuts screwed on at each end.

The telescopes are fastened to the fixed disks and are shown in fig. 4. X is the collimator with the slit, Y the observing-telescope, and Z the collimator with the micrometer. The position of the micrometer and the form of the prism opposite the observing-telescope is explained in the Philosophical Magazine for April 1876, "A New Arrangement for the Micrometer of the Automatic Spectroscope," fig. 3. Part of each moving disk has to be cut away to allow space for the telescopes and fixed prism. This can be done, without removing any useful part, in the way shown in figs. 3 and 4.

The edge of one of the fixed disks is graduated, as shown in fig. 4; and the nearest moving disk carries a vernier, the zero of which for the position of the scale given in the figure must be in the direction K T. It is convenient to mark 5° of circumference as 1° of graduation, since the disk moves five times as fast as the prisms open out from one another. The reading may then be made to give the angle between consecutive prisms. Motion can be given to the instrument by connecting the moving and fixed disks by a rack and pinion.

It may be necessary to adopt some contrivance for keeping the pins always pressing against the same sides of the slits through which they pass. I ensure pressure against the inner sides of the curved slits in the disks by fixing pegs in the disks somewhat in the positions α, β, γ, δ in fig. 3, and passing an elastic band round each pin and the corresponding peg. The bands and pegs are placed on the sides of the disks remote from the prisms, so as not to interfere with the rest of the machinery. To ensure pressure always against the same sides of the slits in the arms, a peg is inserted at E in the fixed disk, fig. 4, and pegs are inserted at F, G, H, I in the arms; the pins P, Q, R, S are connected with the pegs E, F, G, H respectively by elastic bands; and thus the pins P, Q, R, S are drawn round K in one direction, and the arms K P, K Q, K R are drawn in the opposite direction. It will be found that there is not much variation in the length of the band. In order to pull the arm K S by a band which shall not vary much in length, a slit whose middle line is $r = \mathrm{F}\left(\frac{\theta}{n}\right)$ should be cut in each of the fixed disks, and a slit $r = \mathrm{F}\left(\frac{\theta}{0}\right)$ (that is, a straight slit along the initial line K T) should be cut in each of the moving disks; then, if T be a pin passed through these slits, T will be at the same distance from K as the other pins, and a band round T and I will be of the same length as the other bands. This additional pin is not given in the model exhibited; but one of the bands connects an arm with a fixed point, and therefore undergoes a good deal of stretching, which it is better to avoid.

The form of $\mathrm{F}(\theta)$ is arbitrary; but there is an advantage in giving it the form $ae^{-l\theta}$, so as to make $r = \mathrm{F}(\theta)$ an equiangular spiral. Since all the curves will be of the form $r = ae^{-l\frac{\theta}{m}}$, they will all be equiangular spirals; and therefore in fig. 1 the angle A P p will be constant, and the angle d P p will also be constant, and consequently the angle A P d will be constant. Similarly it may be shown that the angles B Q c,

C R b, D S a are constant; and by the symmetry of the figure we see that A P d = D S a, and B Q c = C R b. From the equations to the curves we get $\tan \text{A P } d = \frac{5l}{l^2-4}$, and $\tan \text{B Q } c = \frac{5l}{l^2-6}$; and as it will be best to have the intersections as nearly as possible at right angles, we must make one of these angles exceed a right angle by just as much as the other falls short of one. This gives $\tan \text{A P } d + \tan \text{B Q } c = 0$, or $l = \sqrt{5}$. The equations to the curves now become

$$r = ae^{-\theta\sqrt{5}}, \quad r = ae^{-\frac{\theta}{2}\sqrt{5}}, \quad r = ae^{-\frac{\theta}{3}\sqrt{5}}, \quad r = ae^{-\frac{\theta}{4}\sqrt{5}}.$$

From these equations we have

$$\text{A P } p = a \text{ S } s = \tan^{-1}\frac{1}{\sqrt{5}} = 24^\circ\ 6'$$

$$\text{B Q } q = b \text{ R } r = \tan^{-1}\frac{2}{\sqrt{5}} = 41\ 48$$

$$c \text{ Q } q = \text{C R } r = \tan^{-1}\frac{3}{\sqrt{5}} = 53\ 18$$

$$\text{A P } p = \text{D S } s = \tan^{-1}\frac{4}{\sqrt{5}} = 60\ 48$$

Hence

$$\text{A P } d = \text{D S } a = 84\ 54$$

$$\text{B Q } c = b \text{ R C} = 95\ 6$$

so that the intersections of the slits in the disks only differ about 5° 6′ from right angles.

In the model, a was put = 25, and the position of points in the fourth curve were calculated from the equation $r = 25e^{-\frac{\theta}{4}\sqrt{5}}$ by first transforming this equation into the form

$$r = \log^{-1}\{1{\cdot}397940 - \tfrac{1}{10}\log^{-1}({\cdot}385209 + \log\theta)\},$$

and thence obtaining r for every degree in the value of θ. The first, second, third, and fifth curves were obtained by putting $\frac{1}{4}$, $\frac{2}{4}$, $\frac{3}{4}$, and $\frac{5}{4}$ of the value of θ against the same value of r. The limits between which the curves must be drawn will depend on the refractive power of the glass employed for the two ends of the spectrum. In the model the angle between consecutive arms varies between 45° and 54°.

The following Table gives the calculated points in the series of curves:—

Angle, 1st curve.	Angle, 2nd curve.	Angle, 3rd curve.	Angle, 4th curve.	Angle, 5th curve.	Radius, in inches.
° ′	° ′	° ′	°	° ′	
45	90	135	180	225	4·318
45 15	90 30	135 45	181	226 15	4·276
45 30	91	136 30	182	227 30	4·234
45 45	91 30	137 15	183	228 45	4·193
46	92	138	184	230	4·152
46 15	92 30	138 45	185	231 15	4·112
56 30	93	139 30	186	232 30	4·072
46 45	93 30	140 15	187	233 45	4·033
47	94	141	188	235	3·994
47 15	94 30	141 45	189	236 15	3·955
47 30	95	142 30	190	237 30	3·917
47 45	95 30	143 15	191	238 45	3 879
48	96	144	192	240	3·841
48 15	96 30	144 45	193	341 15	3·804
48 30	97	145 30	194	242 30	3·767
48 45	97 30	146 15	195	243 45	3·730
49	98	147	196	245	3·694
49 15	98 30	147 45	197	246 15	3·658
49 30	99	148 30	198	247 30	3·622
49 45	99 30	149 15	199	248 45	3·587
50	100	150	200	250	3·552
50 15	100 30	150 45	201	251 15	3·517
50 30	101	151 30	202	252 30	3·483
50 45	101 30	152 15	203	253 45	3·449
51	102	153	204	255	3·415
51 15	102 30	153 45	205	256 15	3·382
51 30	103	154 30	206	257 30	3·349
51 45	103 30	155 15	207	258 45	3·316
52	104	156	208	260	3·284
52 15	104 30	156 45	209	261 15	3·252
52 30	105	157 30	210	262 30	3·220
52 45	105 30	158 15	211	263 45	3·189
53	106	159	212	265	3·158
53 15	106 30	159 45	213	266 15	3·127
53 30	107	160 30	214	267 30	3·097
53 45	107 30	161 15	215	268 45	3 068
54	108	162	216	270	3·039

176 Haverstock Hill, London.

XIII. *On a Repetition of* Dr. Kerr's *Magneto-optic Experiment.*

To the Editors of the Philosophical Magazine and Journal.

GENTLEMEN,

ON reading the very remarkable paper by Dr. Kerr, "On Rotation of the Plane of Polarization by Reflection from the Pole of a Magnet," in the Philosophical Magazine for May 1877, it occurred to me that by the aid of some apparatus which I had by me I might be able to reproduce the phenomena on a somewhat larger scale than in the original experi-

ments. This expectation has been so far fulfilled that I think a short account of the experiments may not be uninteresting to your readers.

The magnet consisted of a bar of soft iron 2 feet 2 inches long and $2\frac{1}{4}$ inches in diameter, on which were two helices containing each about 1030 turns of wire. It was excited by ten quart Grove cells arranged in series. The submagnet consisted of a wedge of soft iron 5 inches long by 2 inches thick at the wide end, and having an edge $2\frac{1}{4}$ inches long.

The magnet being placed *horizontally*, the submagnet was brought up against its polished end, but prevented from touching it by two pieces of copper "bell"-wire. The light of a paraffin-lamp was polarized by a large Nicol's prism and allowed to fall on the pole at about 45°. The reflected light was examined by the Jellett analyzer described by me in the Philosophical Transactions for 1877, part 1. The effect was most marked and distinct.

The following readings of the plane of polarization were taken:—

Current direct.	Current reversed.
271° 55′	271° 30′
271 57	271 27
271 54	271 28
271 52	271 26

Mean double rotation ... 26′ 45″

I have not as yet been able to get any distinct effect without the submagnet. Until this can be done, "absolute" measures of the amount of rotation due to a given strength of pole will not be possible.

J. E. H. Gordon.

Pixholme, Dorking.

XIV. *On a Case of Lightning; with an Evaluation of the Potential and Quantity of the Discharge in Absolute Measure.* *By* R. S. Brough*.

THE south-west monsoon of 1871 may be considered to have been characterized in the neighbourhood of Calcutta no less by its copious and protracted rainfall than by the violence and frequency of its thunderstorms. During the progress of

* Communicated by the Author, having been read before the Asiatic Society of Bengal on the 7th of February, 1877.

one of these storms in the early part of the monsoon, one of the trees standing near the gate of the compound of the building then occupied by the Sadr Diwáni Adálat, and now used as the European Military Hospital, in Lower Circular Road, was struck by lightning. The branches of this tree overhung the wires of the telegraph-line, from which they were only about a foot distant. The discharge passed from the tree to the wires (of which there are four), broke fourteen double-cup porcelain insulators, and passed to earth through the iron standards on which the wires are supported.

The one ends of all the four wires were connected to earth through instruments in the Calcutta Telegraph office, at a distance of about 5½ miles from the locality of the accident. The other ends were connected as follows to earth through instruments—the first at the Telegraph workshops (a distance of less than ¼ mile), the second at the Lieutenant-Governor's residence (less than ½ mile), the third at Atchipur (less than 14 miles), and the fourth at Diamond Harbour (less than 25 miles). At the moment of the discharge nothing extraordinary was noticed at any of these offices.

It is often far too generally stated in text-books that lightning invariably follows the best conductor to earth. This statement is misleading at the best, and is absolutely untrue if the word "conductor" be employed in the sense to which it is usually restricted in electrical science. In this instance, for example, we find that the lightning broke fourteen insulators, each having probably an electrical resistance of several thousand megohms, in preference to traversing a wire-resistance of not more than 500 ohms to earth through the receiving-instrument in the telegraph-workshops. The writers appear to overlook the fact (experimentally illustrated long ago by Faraday) that there is exerted a mechanical stress proportional to the square of the potential tending to produce disruptive discharge, as well as an electromotive force proportional to the simple potential tending to produce a conductive discharge. Thus the discharge may occur either along a path of minimum mechanical resistance or along a path of minimum electrical resistance. Which form of discharge will occur in any particular instance depends, of course, on the special circumstances of the case; but, generally speaking, as the potential increases, the tendency naturally is, *cæteris paribus*, for the disruptive to predominate over the conductive. In the case of lightning the potential is so great, that, for any form of "lightning-protector" to be efficient, the conductive facilities offered must be correspondingly great; that is, the protector must offer no sensible resistance to earth, otherwise a disrup-

tive discharge may take place from the protector itself, which under these circumstances becomes merely a source of danger*. This tendency to disruptive discharge is taken advantage of to protect telegraph-instruments from lightning. An earth-wire is brought very near to the line-wire, from which it is insulated by only a very thin stratum of air; when the potential of the line-wire rises abnormally, a disruptive discharge takes place at this point, and the receiving-instrument is thus saved.

I have twice lately seen it stated that Sir W. Thomson found that the resistance of air to disruptive discharge decreased as the thickness of the stratum increased; and a French writer has referred the possibility of the occurrence of lightning discharges several kilometres in length to this cause. Sir W. Thomson's earlier experiments certainly showed this unexpected result, probably due to the minute distances at which he was operating; but a later series of experiments, made at larger distances, showed this result in a much less marked degree; and Sir W. Thomson himself says, "it seems most probable that at still greater distances the electromotive force will be found to be sensibly constant, as it was certainly expected to be at all distances" †.

Another assertion of the text-books is that the metallic rods now employed as lightning-protectors on buildings do not "attract" lightning. This statement is literally true, according to the meaning of the word "attract," but is untrue in effect; for such a rod lightning-protector determines a line of maximum induction, and a discharge is more likely to occur at the place than if the protector were not there. Professor Clerk-Maxwell does not appear to hold this opinion; but it seems to me unquestionable that if a charged thunder-cloud, driving before the wind, is carried over a building furnished

* It is very necessary, therefore, that all systems of lightning-protectors should be tested for resistance from time to time. Mr. Schwendler's method of quantitatively testing "earths" has already been described before the Society (Journ. As. Soc. of Bengal, part 2, vol. xl. 1871). In this method two temporary auxiliary earths are required. Calling the resistance of the lightning-discharger earth x, and that of the auxiliary earths respectively y and z, the three resistances $x+y=a$, $x+z=b$, and $y+z=c$ are measured by any accurate method most convenient (*e. g.* Wheatstone's bridge, differential galvanometer, tangent- or sine-galvanometer, &c., or even an empirically calibrated galvanoscope), the mean of positive and negative readings being taken to eliminate any natural electromotive force between the earths. From the results thus obtained the unknown resistance x can be calculated by the formula

$$x=\frac{a+b-c}{2}.$$

† Papers on Electrostatics and Magnetism, p. 259.

with a lofty metallic rod, discharge is more likely to occur than if the rod were away. In proof of this I may refer to the case reported by Mr. Pidgeon in 'Nature,' and subsequently discussed before the Society of Telegraph Engineers (Proceedings, May 12, 1875), in which the flagstaff acted the part of an ordinary "lightning-protector."

Professor Clerk-Maxwell observed, in his paper recently read before the British Association at Glasgow, that such lightning-protectors are designed rather to relieve the charged cloud than to protect the threatened building. In fact lightning-rods are legitimately employed for this very purpose in the vineyards, where the object in view is to relieve charged clouds and prevent disruptive discharges and the consequent showers of hail.

Under ordinary circumstances, however, the noise and light of the lightning-flash must be regarded as a very harmless, if disagreeable, way of getting rid of some of the potential energy of electrical separation.

The protection of cities on the same principle, even if necessary or desirable, would be too expensive and unsightly ever to be put in practice. But Faraday has proved that if our houses were made of metal, they would constantly remain at the potential of the earth, we should virtually be "underground," and live within them in perfect security. The iron churches occasionally employed in Europe fulfil this condition exactly. It is not, of course, usually practicable to live in metal houses; but we can live in almost equally effective metal cages formed by running conductors connected to earth along the summit, eaves, and corners of our houses*.

The usual rod protectors appear to be only suitable to such structures as themselves determine lines of maximum induction, *e. g.* church-spires, factory-chimneys, flagstaffs, &c.

The case of lightning referred to at the beginning of this paper is of peculiar interest, because we know precisely the mechanical effect produced by the flash, and from this we can work back and estimate roughly the potential and quantity of the electrical discharge.

In the first place we can calculate the force required to burst the cylindrical portion of the porcelain insulator into which the iron stalk is cemented.

Let r = radius of the inside of the cylinder,

R = „ outside „

and F = the resistance to bursting;

* This portion of the paper was written before the Meeting of the British Association at Glasgow.

then

$$F = f\frac{R^2 - r^2}{R^2 + r^2},$$

where $f = 66 \times 10^4$ grammes on the square centimetre.

Now the line-wire was bound to the insulator by a thinner wire passing round it. The surface-density could not have been uniform round the binding wire, but must have been greatest on the side touching the insulator.

By the method of electrical images in two dimensions it may be shown that the surface-density (σ) on the inner side of the binding wire is approximately

$$\sigma = \frac{Q}{4\pi^2 R\sqrt{d-a}(\sqrt{d+a}-\sqrt{d-a})},$$

where Q is the total charge on the binding wire, d the distance of the binding wire from the stalk of the insulator, and a the radius of the binding wire. But

$$2\pi\sigma^2 = F,$$

$$\therefore\ \sigma = \sqrt{\frac{F}{2\pi}};$$

whence

$$Q = \sqrt{\frac{F}{2\pi}} \cdot 4\pi^2 R\sqrt{d-a}(\sqrt{d+a}-\sqrt{d-a}),$$

which is the expression for the quantity of the charge on one insulator. As there were fourteen insulators broken, this result must be multiplied by fourteen in order to obtain the total quantity of the discharge.

Again, the electrostatic capacity of the binding wire is

$$S = \frac{2\pi R c}{\log_\epsilon \dfrac{d+\sqrt{d^2-a^2}}{d-\sqrt{d^2-a^2}}},$$

where $c = 1{\cdot}9$ about.

But $VS = Q$;

$$\therefore\ V = \frac{Q}{S} = \sqrt{\frac{F}{2\pi}} \cdot \frac{2\pi}{c}\sqrt{d-a}(\sqrt{d+a}-\sqrt{d-a}) \times \log_\epsilon \frac{d+\sqrt{d^2-a^2}}{d-\sqrt{d^2-a^2}},$$

which is the expression for the potential of the discharge.

Now, in the particular case under consideration,

$r = 1{\cdot}500$ centim.,

$R = 3{\cdot}000$ centims.,

$d = 2{\cdot}250$ „

and $a = 0{\cdot}125$ centim.

Hence $F = 396 \times 10^3$ grammes per square centimetre,

$14Q = 50586{\cdot}5$, $V = 722{\cdot}7$ } absolute electrostatic C.G.S. units.

Changing the units to the ordinary ones in practical use, we find

$14Q = 16{\cdot}86$ microfarads,

$V = 216810$ volts.

Assuming the sparking-distance to increase as the square of the potential, it can be calculated from the experimental results obtained by Messrs. Warren De La Rue and Müller (Proc. Roy. Soc. Jan. 1876), namely that 1000 rod-chloride-of-silver cells give a spark 0·009166 inch, that a difference of potentials of 216,810 volts would produce a spark in air between two electrodes at a distance of about 36 feet apart. This is, of course, a relatively very short distance ; but it must be remembered that we have only taken into consideration that portion of the energy of the discharge which was employed in breaking the fourteen insulators, and have neglected all that was spent in heat, light, &c.

XV. *On the Nature of what is commonly termed a "Vacuum."* By S. Tolver Preston.

1. IT may perhaps not be uninteresting to consider what light the researches of Professor Maxwell on molecular distances in connexion with the kinetic theory of gases, and those of Sir William Thomson and others, are capable of throwing upon the physical condition of what is ordinarily termed a "vacuum." This inquiry might have an additional interest at the present time, when experiments with extremely rarefied media in connexion with the radiometer and the discharge of electricity in evacuated tubes are going on, and certain inferences regarding the condition of "vacua" would lead one to infer that a prevalent idea may exist regarding the state of a "vacuum" (so termed) which is not consistent with facts, as indeed I am not aware that any special investigations have been made on this subject. I make no pre-

* Communicated by the Author.

tence to do more than apply the mathematical results of others to a special case; and I shall be glad if the result obtained is of any service, or may induce others to pursue the subject further.

2. It has been deduced by Professor Maxwell (Phil. Mag. Dec. 1873) that the number of molecules contained in a cubic centimetre of any gas at normal density may be estimated, in round numbers, at 19 million billions. This is carefully given by Professor Maxwell as a *probable* or approximative result. But, on the other hand, it should be kept in view that the result is estimated on the basis of experimental data; and other results predicted by mathematics in connexion with the kinetic theory, and which admit of direct test by experiment, have (as is well known) been confirmed in a striking manner. Also it is needless to add that mathematics is not less certain because the dimensions dealt with are small. Sir William Thomson in a paper on "Atoms," published in 'Nature' (March 31st, 1870), by four distinct lines of argument arrives at accordant results as limiting values for dimensions of molecular structure; and these results agree very well with the above estimate of Professor Maxwell. Sir William Thomson finally remarks that the results may be considered as established with "a very high degree of probability."

3. Taking, therefore, Professor Maxwell's result in reference to a gas, if we take the cube root of the number of molecules contained in a cubic centimetre, or $\sqrt[3]{19 \times 10^{18}}$, we have the number of molecules which (placed at their mean distances) would reach the length of a linear centimetre, or we have 2,668,400. The mean distance of the molecules of a gas at normal density is therefore $\frac{1}{2,668,400}$ of a centimetre, about one seven-millionth of an inch—which, it may be remarked, is about one seventh of the distance capable of being measured by a Whitworth machine. We have now to consider what the effect is on rarefying the gas. To clear the ideas, suppose all the molecules in a given space (such as an air-pump receiver) to be placed regularly; *i. e.*, suppose the given space to be subdivided up into a number of imaginary cubes of such a size that, when molecules are placed at the corners of all these cubes, exactly the whole number of molecules is thus taken up. Then the side of one of these cubes will be one seven-millionth of an inch long, representing the mean distance of the molecules. Rarefying a gas to a given degree is of course equivalent to increasing the space in which the gas is to that same degree. The side of a cube being as the cube root of its volume, it follows that when the gas is

rarefied, which is equivalent to increasing the volume of space occupied by it, the side of any cube (representing the mean distance) will be increased in the ratio of the cube root of the number of times the gas is rarefied. In order to take an extreme case, let us suppose the gas to have been rarefied a million times (*i. e.* to one millionth of its normal density) this corresponding to about $\frac{1}{33,000}$ of an inch of mercury, a measure that would be imperceptible on an ordinary barometric gauge. After this degree of rarefaction the mean distance of the molecules will have been increased to a hundred times, or $\sqrt[3]{1,000,000}$. The mean distance of the molecules, after rarefying a million times, will therefore be about one seventy-thousandth of an inch, a dimension which, if plotted on a scale, would be invisible to the eye. It follows, therefore, that even with this extreme degree of rarefaction (supposing it could be attained with a good mercurial pump), the molecules of gas are still packed so close that their distance, if marked on a scale, would be invisible to the eye, and still 19 billions (dividing the number originally contained in a cubic centimetre by 1,000,000) of them are enclosed in a cubic centimetre. This may possibly not harmonize with the general idea of what is called a "vacuum." Indeed it may be fairly questioned whether the inconceivable number of 19 billion separate existences accumulated in the narrow limits of a cubic centimetre of space may not be properly regarded as something the very opposite of a "vacuum." The *size* of a molecule may not be of so much influence. Its *presence* may be the main thing. The presence of 19 billion separate portions of matter in a cubic centimetre of space may conceivably produce an effect on an electric discharge or a radiometer very different from a vacuum. One reason why the distance of the molecules of gas increases with such extreme slowness on rarefying is evidently due to the fact that the distance only increases as the cube root of the number of times the gas is rarefied. If it were imagined to be possible to carry the rarefaction a million times as far as the above extreme limit, there would still be 19 million molecules in a cubic centimetre.

4. It may therefore be truly said that even the best pump does not increase appreciably the distance of the molecules of gas, inasmuch as the distance moved through by the molecules of gas under the action of the pump, if plotted on a scale, would be inappreciable to the eye; or, in other words, when the most powerful pump has done its work, the molecules of gas are still so close that their distances are too small to be

visible on any scale, and the number of molecules of residual gas contained even in a cubic centimetre of space may be reckoned by billions. In the case of what would be regarded as an ordinary "good vacuum," such as that used in Geissler's vacuum-tubes for electric discharges (say, 0·7 of a millimetre of mercury, or a rarefaction of one thousandth), the distance shifted through by the molecules under the action of the pump in the act of rarefying would be only about $\frac{1}{778000}$ of an inch, and the number of molecules in a cubic centimetre of the residual gas 19 thousand million millions (a cubic centimetre being about one fourteenth of a cubic inch).

5. It may perhaps be of interest to consider what effect the rarefaction has upon the mean *path* of the molecules of gas, the mean path being the mean or average distance moved through by a molecule before coming into collision with another molecule. The mean path of the molecules of several well-known gases has been calculated by Professor Maxwell from some carefully executed diffusion-experiments by M. Loschmidt. The mean path of a molecule of hydrogen at normal density is given at ·0000965 of a millimetre, or about $\frac{1}{263200}$ of an inch. Loschmidt has deduced the following proportion:—"*As the volume of a gas is to the combined volume of all the molecules contained in it, so is the mean path of a molecule to one eighth of the diameter of a molecule.*" The mean path of a molecule therefore increases directly as the number of molecules in the unit volume of the gas is diminished. The mean path accordingly increases directly as the number of times the gas is rarefied. The value of the mean path therefore augments, on rarefying, at a disproportionately greater rate than that of the mean distance of the molecules of gas.

6. It appears to have been assumed in certain radiometric experiments that the mean path of the molecules of the residual gas is comparable to the diameter of the bulb of the radiometer itself. In a paper by Mr. Crookes which appeared in the 'Philosophical Magazine' for June last, is the following passage:—"But when the exhaustion is carried to so high a point that the molecules are sufficiently few, and the mean length of path between their successive collisions is comparable with the dimensions of the vessel." This is also assumed in a paper by M. Finkener in Poggendorff's *Annalen* on the subject of the radiometer, where the assumption is made that the gas is rarefied so far that the mean length of path of the molecules is very great compared with

the dimensions of the ball of the radiometer*. Conceivably these assumptions may naturally arise from the idea that in a "vacuum," so termed, the molecules of gas are few and widely scattered. This, we have shown, is by no means the fact. It may therefore be worth while investigating from the above result of Professor Maxwell what the mean path of the molecules of gas is at the degree of rarefaction at which the rotation of the radiometer was observed to be at a maximum. This maximum is stated in Mr. Crookes's paper to have occurred in the case of hydrogen at a rarefaction of 50 millionths. The mean path being in direct proportion to the rarefaction, its value in this case will be $\frac{1}{263\frac{1}{200}} \times \frac{1000000}{50} = \frac{1}{13}$ of an inch about. This is but a small fraction of the diameter of the bulb. It is remarked that the special gauge used could not indicate the pressure of the mercury vapour of the pump, and that therefore the actual values for rarefaction attained might have been somewhat under the estimated values. This would go to make the mean length of path, when the rotation was at its maximum, a still smaller fraction of the diameter of the bulb than above; and it is stated that at higher rarefactions the rotation notably began to fall off. The length of path of the molecules of other gases is also less—about half that of hydrogen. My object here is not in any way to deal with the cause of the rotation of the radiometer, but rather to adduce from the best obtainable data certain facts which may tend to throw a light upon the true physical condition of the rarefied gas enclosed in the instrument; and it is certain that, whatever the true explanation may be, it cannot be otherwise than forwarded by such a course.

London, June 1877.

XVI. *Ice as an Electrolyte.* *By* W. E. Ayrton *and* John Perry, *Professors in the Imperial College of Engineering, Tokio, Japan*†.

[Plate II.]

FOR the purpose of measuring the resistance of ice at various temperatures, its power to act as an electrolyte, and its specific inductive capacity, the following piece of apparatus was constructed. A B C D (Plate II. fig. 1) is a copper box 17·4 centims. in diameter, rigidly fixed by means of

* "Wir verdünnen das Gas so weit, dass der Weg, den ein Molecül zwischen zwei Zusammenstössen mit anderen Molecülen durchschnittlich zurücklegt, sehr gross ist im Verhältniss zu den Dimensionen der Kugel des Radiometers." (Pogg. *Ann.* July 1876, part 8, p. 579.)

† Communicated by the Physical Society.

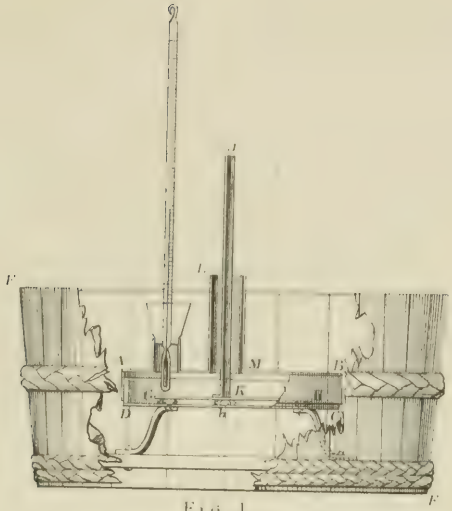


Fig. 1
Ice as an Electrolyte

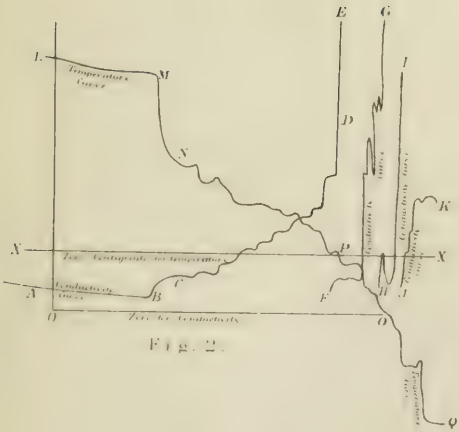


Fig. 2.

Fig. 3.

three legs in the inside of a wooden tub F F. Resting on the bottom of the copper box, but separated from it by three small pieces of glass (*a*) (*b*) (*c*), is a copper disk, G H, 13 centims. in diameter, to which is fastened a copper strip J K. The box is closed by a very tightly fitting cover furnished with two openings—one, L M, to allow J K to pass through without touching the cover, the other for the admission of a thermometer. Distilled water having been introduced into the copper box to a sufficient depth to cover the disk G H, the temperature could be lowered by the introduction of a freezing-mixture of snow and salt inside the tub above and below the copper box, great care being taken that none of the mixture fell into the box through the tube L M, which was necessarily left open.

I. *Preliminary experiments.*—The current from one Meidinger cell was passed through the ice and a reflecting-galvanometer, the space between the copper plates being 2 millims. Keeping the temperature nearly constant (it varying between $-18°{\cdot}2$ and $-17°{\cdot}2$ C.), we found that in one hour the galvanometer-readings increased from 46·8 to 168·8, corresponding to a diminution in resistance per cubic centimetre of the ice from 354 megohms to 98 megohms. The cause of this may have been that, with such thin glass separating the copper disk from the box, some tilting may have occurred at freezing, so that the coppers were not perfectly parallel; or it may have been due to a very little of the salt water of the freezing-mixture having found its way into the copper box by passing between the box and the cover. The box was therefore opened and cleaned, fresh distilled water put in, and the cover cemented to the box by "cap-cement" to avoid the possibility of the salt water entering the box.

II. The current from eighty-seven porous Daniell's cells joined in series was passed through the ice, the temperature being kept very nearly constant at $-8°{\cdot}0$ C. The galvanometer-reading fell regularly from 28·5 to 12·73 in twenty-seven minutes, being equivalent to an apparent rise in the resistance per cubic centimetre of the ice from 3767 megohms to 8443 megohms. The temperature remaining constant, the reading fell to 7·20 in about two hours, corresponding with a specific resistance of 17,310 megohms. Disconnecting the battery and joining the coppers on the two sides of the ice through the galvanometer, a discharge-current, which rapidly diminished, was obtained, as was to be expected.

Further experiments showing the difficulty of maintaining the copper disk approximately parallel to the bottom of the

box, the three pieces of glass were removed and thicker pieces, 0·324 centim. thick, put in their place. The cover was again cemented to the box, this being, in fact, always carefully done after each occasion on which it was necessary to open the box.

III. Temperature being 2°·4 C., an electromotive force of 0·0087 volt gave (after waiting eleven minutes to allow the current to overcome any previous polarization) a deflection of 212, corresponding with a resistance of 355,000 ohms per cubic centimetre. Allowing the temperature to fall slowly, we found the readings to remain pretty steady for thirty-four minutes when the temperature had become −0°·6 C. From this time there was a moderately rapid increase of resistance up to 14 megohms per cubic centimetre after forty-three minutes, the temperature now being −3°·8 C. The deflection was now 54 ; and we increased the battery ten times, when it was found that this increase of the battery did not increase the deflection proportionately (although subsequent experiments showed that the deflection was very approximately proportional to the current); in fact, making the battery ten times as large (that is, now using an electromotive force of 0·087 volt), only gave a deflection of 129. The battery was now immediately reduced to an electromotive force of 0·0087 as before ; but the deflection was now only 28. Leaving on this electromotive force, the deflection was observed to steadily diminish until at last it became negative ; and it eventually required an electromotive force of 0·0435 volt to bring the spot of light to zero. This electromotive force in the ice, which appeared to be developed by the employment of an electromotive force of 0·087 volt for only about one minute, remained quite constant, and continued to balance an electromotive force of 0·0435 volt for about half an hour, when, the apparatus having been cooled down, a larger electromotive force was now employed.

An electromotive force of	gave a deflection of	at a temperature of
0·087 volt	9·5	−5°·1 C.
0·174 „	19·5	
0·261 „	27·7	−6°·4 C.
	diminishing to 23·5 in thirteen minutes	

These deflections are nearly proportional to the electromotive forces.

An electromotive force of 2·61 volts	gave a deflection of 52·5 diminishing to 30·1	at a temperature of −8°·3 C.
Now suddenly increasing this to 4·35 volts	the deflection diminished to 39·5	−8°·3 C.

It might have been expected that doubling the electromotive force would have more than doubled the deflection, since the diminution of resistance in a dielectric produced by time of charging only proceeds gradually—whereas the deflection only increased from 30·1 to 39·5. This peculiarity is shown more fully in the following Table, in which the readings just before and after changing the battery-power are given, the intermediate ones being omitted:—

Electromotive force 2·61 volts.

Time.	Deflection.	Temperature.
h m s		
7 48 30	30·1	−12° C.

Electromotive force of battery increased to 4·25 volts.

7 49 30	39·5	−12° C.
7 51 30	36·5	

Electromotive force increased to 8·7 volts. First swing off the scale, but very soon grew steady on returning.

7 52 0	53·1	−12°·2 C.
7 53 0	50·5	
7 54 0	49·1	

Electromotive force increased to 17·4 volts. First swing off the scale.

7 55 0	72·7	−12°·5 C.
7 56 0	69·0	
7 61 0	59·5	

Electromotive force increased to 28·71 volts. First swing off the scale.

8 2 0	76·5	−12°·8 C.
8 5 0	68·6	
8 6 0	67·2	−13°·0 C.

Short-circuited the coppers on the two sides of the ice for four minutes.

Afterwards electromotive force increased to 87 volts. First a great swing off the scale, then returned, and in about one minute—that is, at

h	m	s	Deflection.	Temperature.
8	12	0	212·7	−12°·85 C.
8	15	0	145·7	
9	12	0	66·2	−10°·8 C.
9	17	0	65·2	
9	58	30	66·2	− 8°·85 C.

Comparing the observation at $8^h\ 12^m\ 0^s$ with that taken at $8^h\ 6^m\ 0^s$, we see that the deflections are nearly proportional to the electromotive forces employed; this, however, is not the case in the other instances when the electromotive force was increased. The object of giving three or four time-observations for each electromotive force in the above Table is for the purpose of showing with what rapidity the reading was changing in each case.

IV. *February* 11.—A very consistent series of observations was made. We first tried the effect of varying the time of charging when measuring the discharge from the arrangement as a condenser; and we found that increasing the time of charging increased the discharge, the temperature of the distilled water in the copper box being 8°·7 C. Charging, however, for ten seconds with an electromotive force of 0·174 volt, and discharging through the galvanometer when shunted with the one-thousandth shunt, and leaving the copper disk and box short-circuited for fifteen seconds after each discharge, we obtained, during many successive trials, swings varying between 75 and 81, and having a mean value of 79. This corresponded with a capacity for the water of 1881 microfarads, or 4·384 microfarads per cubic centimetre, making the specific inductive capacity of water 50×10^6, that of air being called unity. Of course this number is rather too low, as no allowance is made for the loss of charge that must occur in the very short interval between the conclusion of the charging and the commencement of the discharge. The current produced by an electromotive force of 0·174 volt was now passed through the water, and the fall of current measured as the temperature was lowered. This diminution of current was partly due to polarization, but more due to increase of resistance by diminution of temperature. It was quite evident that this increase of resistance was very great, and that it was quite regular in the passage from the liquid to the solid state. These observations we do not give; it is sufficient to state that they were consistent with the more important subsequent ob-

servations given below. When the temperature had fallen to $-13°{\cdot}5$ C., we stopped the resistance-tests to take the capacity of the ice. We charged for ten seconds with an electromotive force of 0·174 volt, and short-circuiting the ice for fifteen seconds after each discharge, exactly as was done with the water. We now found, however, that when using the one-thousandth shunt there was no visible motion of the spot of light on discharging; and when no shunt was employed the swings only reached 25. Now, disregarding the error produced by varying the shunt in capacity-testing (a correction for which could be made in the way explained by Mr. Latimer Clark, Journ. Soc. of Teleg. Engineers, vol. ii. 1873, p. 16), and also neglecting the frictional resistance of the air, it follows that the capacity of ice at $-13°{\cdot}5$ C. is to the capacity of water at $+8°{\cdot}7$ C. as 25 to 79,000, or as unity to 3160. This result, however, has to be corrected for the effects of an opposing electromotive force due to some slight oxidation of the copper on the sides of the ice, and which equalled 0·053 volt. Applying this correction, we find the ratio of the capacities to be as unity is to 2240. This makes the capacity per cubic centimetre of ice at $-13°{\cdot}5$ C. to be 0·002 microfarad, and the specific inductive capacity 22,160, that of air being called unity.

Substance.	Approximate capacity per cubic centimetre in microfarads.	Specific Inductive capacity approximately.
Air	8831×10^{-11}	1
Ice at $-13°{\cdot}5$ C.	196×10^{-5}	22160
Distilled water at $+8°{\cdot}7$ C.	4·384	50×10^{6}

This furnishes an additional example of the principle recently pointed out by us, that *low* specific resistance is associated with *high* specific inductive capacity.

For further experiments on the capacity of the ice at different temperatures &c., see further on.

At 12 hours $30\frac{1}{2}$ minutes the current produced by 2·61 volts was passed between the copper plates, the ice being at a temperature of $-13°{\cdot}6$ C. The temperature was allowed to rise very gradually; and time-readings of the galvanometer deflection were taken. From these the curves A B C D E, F G, H I, J K (fig. 2) have been constructed, horizontal distances representing time on such a scale that from the point A to the point E the time was $207\frac{1}{2}$ minutes, and vertical

distances measured from the line O O to the curve A B C D E representing conductivity, the specific resistance per cubic centimetre at B, for instance, being 2240 megohms. F G is a continuation from E one tenth as great for vertical distances (that is, for conductivity), but on the same scale for horizontal distances. Again H I is a continuation from G on a scale one hundredth as great for vertical distances as in the curve A B C D E, and J K on a scale for vertical distances one thousandth as great, the scales for horizontal distances in all the curves being the same. The curve L M N P Q is drawn so that vertical distances measured from the line X X represent temperature, and horizontal distances time—the zero for time, and the length corresponding with one minute, being the same as for all the other curves; negative temperature is represented upwards and positive temperature downwards—the point L corresponding with a temperature of $-13°{\cdot}1$ C.

The current continued to diminish regularly to the point B, when the temperature shown by the point M was $-12°{\cdot}3$ C., and the time 10 minutes past 3. At this point and at the other steep places in the curves, water was thrown into the freezing-mixture to raise its temperature; and at such points as C, where the current had evidently reached a maximum at a corresponding temperature N, the readings are supposed to represent the true conductivities at the corresponding temperatures; but this, of course, is only approximately accurate. It is very striking how the maxima of conductivity and temperature correspond with one another, considering that the thermometer only indicated the temperature of the air in the copper box above the ice, whereas change of current indicates change of state in the ice itself. The very great increase in conductivity which occurs at the melting-point is seen to be quite regular, and unlike what one might expect from the discontinuity of the solid and liquid states.

Taking the corresponding conductivities and temperatures at points C, N, &c., we have drawn the curves R S, T V (fig. 3). Horizontal distances to the right of Y Y represent positive temperatures, and to the left negative, on such a scale that the point R corresponds with a temperature of $-12°{\cdot}4$ C. Vertical distances measured from X X represent conductivity on such a scale that the point R corresponds with a resistance per cubic centimetre of 2240 megohms. T V is a continuation from S on a scale for vertical distances three thousandths of that employed in the curve R S, the scale for temperature remaining as before: the point V thus corresponds with a resistance per cubic centimetre of 0·33 megohm at a temperature $11°{\cdot}02$ C. From the curves (fig. 3) it would appear that the

very great increase in conductivity occurred at about 1° C.; it is possible, however, that the apparently corresponding points of maximum temperature and maximum conductivity shown in the curves (fig. 2) may not have really exactly corresponded, although changes in the temperature always accompanied changes in the current.

The curves R S, T V do not appear to be logarithmic. The coordinates of the points from which they have been drawn are given in the following Table:—

Temperature, in degrees Centigrade.	Resistance per cubic centimetre, in megohms.
−12°·4	2240
− 6·2	1023
− 5·02	948·6
− 3·5	642·8
− 3·0	569·3
− 2·46	484·4
− 1·5	387·6
− 0·2	284·0
+ 0·75	118·8
about + 2·2	24·8
+ 4·0	9·1
+ 7·75	0·54
+11·02	0·34

V. The copper disk G H (fig. 1) was now removed and replaced by a disk of zinc of exactly the same size. The pieces of glass used to separate the zinc disk from the bottom of the copper box were the same as those previously employed, being 0·324 centim. thick. Distilled water was poured in so as to cover the zinc plate, and the cover was cemented on the box as before. In the following experiments, K J (fig. 1) was a strip of zinc cut out of the same sheet as the disk G H and bent up: the strip K J and the disk G H were therefore continuous without joint. The point J was joined to one of the electrodes of a Thomson's quadrant electrometer, and the copper box D C to the other electrode. Both with water and with ice the maximum electromotive force obtained was one volt about.

In the first sets of experiments, A, B, C, the zinc disk and copper box were alternately joined together and insulated from one another, the result of the short-circuiting being, of course, to diminish the electromotive force by polarization. While this was being done the temperature was gradually lowered.

It is rather difficult to determine how much the results were affected by polarization and how much by the lowering of the temperature. We give, however, the results (in a tabulated form) as we obtained them:—

A.

Time of short-circuiting, in minutes.	fl ection immediately on insulating.	Highest deflection.	Time taken to arrive at highest deflection, in minutes.	Temperature, in degrees Centigrade.
¼	.....	240	1st time quickly 2nd time slowly	about 0°
¼	.....	240	3	−4°
¼	.....	207	2	falling gradually.
¼	.....	203	.....	
¼	.....	196	.....	
¼	... ..	190	.....	
¼	.. ...	178	.....	
3	.....	176 diminishing to 89	quickly.	−12°

B.

1	nearly 0	210	8	15° to 1°·5
1	,,	151	9	−1° to −5°·5
1	,,	170	...	−6°

C.

1	184	203	5½	+2°·6
1	184	203	5½	+2°·6
3	168	204	...	+2°·6
7	156	204	...	+2°·6
10	150	167	1	−1°·5 to −2°·7
1	153	175	6	−3° to −3°·5
3	154	179	7	
7	.....	195·5	25	−5° to −9°·5
7	.....	208·5	60	−12°

It is possible that the deflection 208·5 would always have been obtained had the zinc plate been left sufficiently long insulated after short-circuiting. The plate and box, however, were always short-circuited when the rise in the electromotive force had apparently ceased.

To separate, to a certain extent, the effects due to polarization from those due to difference of temperature the following experiments were made. The zinc plate and copper box were alternately short-circuited for two minutes and insulated for two minutes, the temperature being kept constant at +22°·5 C. This being repeated six times, reduced the deflection 231,

obtained at the end of the first two minutes of insulation, to 155, obtained at the end of the last two minutes of insulation. Exactly the same experiment being repeated ten times with ice at a constant temperature of about −17° C., the deflection 212, obtained at the end of the first two minutes of insulation, was only reduced to 203 at the end of the last two minutes of insulation. It would therefore appear from this set of experiments, that the smaller amount of polarization produced by the high resistance of the ice only allowing a small current to flow during the short-circuiting of the zinc plate and copper box was of rather more importance than the solidity of the ice retarding dissipation of polarization.

VI. *Further experiments on the Specific Inductive Capacity of Ice.*—The zinc disk G H (fig. 1) was now removed and the original copper disk replaced. With a charging electromotive force as small as 0·174 volt, we found that, in the case of ice, it was always necessary to carefully correct the swing for the opposing permanent electromotive force existing between the copper disk and the copper box, whereas with water at about +10° C., when using the same charging electromotive force, it was not necessary to make any such correction. Rough measurements gave this opposing electromotive force at −12°·4 C. as 0·017 volt, and showed that as the temperature rose there seemed to be a regular decrease: at 0° C. it was only 0·003 volt, and at higher temperature it was immeasurably small by the rough method we employed. To avoid this correction being of so much importance, we used an electromotive force of 0·87 volt to determine the capacity of ice at different temperatures. We did not find that the time of charging or the time of short-circuiting affected our results nearly as much as in the case of water; in fact, the time of short-circuiting our ice condenser between successive tests of its capacity hardly affected the results at all; but during a series of observations, the time of short-circuiting between every two being fifteen seconds, and the time of charging being gradually increased from five seconds up to thirty, the swings increased from 56 to 70 divisions of the scale. We therefore, as on the former occasion, always charged for ten seconds and short-circuited for fifteen. Four or five consecutive observations of this kind always showed a slight increase from the first to the last, the temperature being kept quite constant. Several series at different temperatures are shown in the following Table:—

Time.	Temperature, in degrees Centigrade.	Swings, first and last of a series of four.
h m	°	
9 20	−9·5	61 61·5
9 25	−8·8	57 61
9 30	−7·7	58 60·5
9 37	−3·5	57 62·5
9 44	−2·5	60 61
9 55	0	47·5 52·5

In the above experiments the ice condenser always remained short-circuited while the temperature was being raised between each set of experiments. The results obtained appear to show that the specific inductive capacity of ice does not materially alter from −9°·5 C. to −2°·5 C.; the apparent change near the melting-point is very probably due to the increased conductivity of the ice allowing much of the charge to be lost before the discharge through the galvanometer. Our preceding experiments have shown that the conductivity of $\left\{\begin{matrix}\text{ice}\\\text{water}\end{matrix}\right\}$ increases regularly *without discontinuity* from −10° C. to +10° C., although altering very rapidly at 0° C., where the change of state occurs. The specific inductive capacity, on the other hand, appears to change very little while the dielectric (ice) is solid, and perhaps also changes very little while the dielectric (water) is liquid. It must therefore probably undergo a great change at the melting-point, since we have shown that the specific inductive capacity of water at 8°·7 C. is about 2240 times that of ice at −13°·5 C. The specific inductive capacity seems therefore to be a stress and strain phenomenon, and to be intimately connected with the rigidity of the body; whereas the connexion between conductivity and rigidity seems to be less marked. This, we think, bears out all recent theories in molecular physics. The complete investigation of the connexion between the conductivity and specific inductive capacity of $\left\{\begin{matrix}\text{water}\\\text{ice}\end{matrix}\right\}$ at different temperatures will form the subject of a second paper.

March 22, 1877.

XVII. *Notes on the Theory of Sound.* *By* R. H. M. Bosanquet, *Fellow of St. John's College, Oxford.*

[Continued from p. 39.]

6. *The Unsymmetrical Divergence of Sound in Air.*

THE most complete example of unsymmetrical divergence is formed by a disturbance, covering an element of surface so small as to be sensibly plane, advancing through the air with lateral expansion, so that its edges trace out a cone of small vertical angle.

It has generally been assumed that when sound issues from the end of a tube whose diameter is small compared with the wave-length, it diverges after a time in an approximately spherical form. Helmholtz, for instance, assumes that at considerable distances from the orifice the motion may be expressed by the velocity potential of symmetrical spherical (or sectorial) divergence. I have endeavoured to pave the way in the examination of the details of the action by an experimental study of the motion of the air in the case of uniform flow from the end of a pipe; and in the case of outward flow it is quite clear that no approximation to a symmetrical divergence takes place at any moderate distance from the orifice.

It is clear that, according to the rigorous treatment of symmetrical spherical divergence in Part I., the motion in the case of a periodic slowly changing flow is ultimately of the same nature, at any given instant, as that of a steady flow. The general reasoning by which the similarity of the two motions at any instant was independently deduced in that case holds also in this.

Under these circumstances we may treat the phenomena of steady flow, which are easily observed in a rough manner, as affording information as to the nature of the motion in the case of a periodic flow whose wave-length is great in comparison with all the dimensions concerned. The cases of air issuing from and entering the orifice of a tube present different forms. First, as to air issuing from an orifice.

The simplest way of observing the form of motion of the issuing air is to blow smoke out from the rounded aperture of the mouth with a slight but steady pressure. The issuing smoke in this case forms a cone whose vortical angle is somewhere about 20° to 30°. Vertical movements take place which we leave out of consideration.

An india-rubber tube was attached to an acoustic bellows and caused to give forth from its end a horizontal blast. The pressure used was that of the bellows alone with all weights

removed—say half an inch of water. The motion in the surrounding air was explored first with a candle-flame, and then with a pendulum formed by a piece of light fluff attached to a thread. The latter means proved far the most sensitive. The motion consisted of a forward blast occupying a cone of vertical angle 20° to 30°, the outer air *streaming towards the cone from all sides.* The inclination of the stream to the axis of the tube is approximately half that of the radius vector from the end of the tube to the point—the inclination of the stream being *nil* at points close to the tube itself, about 45° at points in the plane of the mouth, and nearly at right angles to the prolonged axis of the tube where the stream joins the outward blast. The phenomenon is that familiar as the origin of the steam blast, and in connexion with a well-known problem in hydrodynamics.

When the flame was placed close to the pipe, a short distance behind the mouth, it curled over and bent towards the mouth in such a way that it was hardly possible to believe that the air was not being drawn in. A tube was then used disconnected from the bellows, and the air alternately drawn in and blown out while the flame was in the above position; the movements of the flame, when suitably placed, were undistinguishable in the two cases. It is therefore clear that we have here a source of transformation, in the case of musical pipes with open ends, by which the octave of the note of the pipe must be formed in the surrounding air. The amount of transformation due to this cause, however, is small; for the currents of this description are very faint.

The case of a tube terminating in a plane or flange was then examined. A brass tube about 2 feet long and 9 inches in diameter was fitted with a flange 6 inches in diameter, through a hole in the centre of which the end of the tube passed. The other end of the tube fitted into the sound-board of the acoustic bellows, by means of which currents of air could be driven through the tube. Burning substances which gave off dense smoke were placed on the flange; and the course of the smoke was watched against a dark background. The issuing air diverged in a cone with vertical angle 20° to 30°.

When the blast was strong enough, a steady horizontal current was maintained along the surface of the flange directed towards the issuing cone; the smoke was carried in by this current and mixed with the issuing air, which then formed a well-defined cone. There was here a source of inaccuracy in the upward tendency of the smoke; there could, however, be little doubt that the currents of the outer air preserved a direction nearly at right angles to the prolonged axis of the tube.

I failed to get any distinct difference in the vertical angle with and without the flange, though it is clear some such difference must exist; I also failed to ascertain any dependence of the vertical angle on the pressure or velocity of issue. Possibly with an apparatus adapted for accurate measures differences of this kind may be shown to exist.

Secondly, as to air sucked into the orifice of the pipe. I have made but few experiments in this case; but there can be little doubt that the currents all tend towards the orifice, and that at a moderate distance the supposition of spherical convergence is approximately applicable to the case without a flange, and that of hemispherical convergence to the case with a flange.

It would appear that the character of the motion is quite different in the two cases. In the case of the issuing air we may regard the motion approximately as being at first the mere impact of a series of disks travelling forward; the amount of divergence I am unable to give any theoretical account of. But when this divergence is once established, it appears as if the motion decomposed itself into two opposite streams of energy—the divergent stream (pressures) travelling forward through its cone, as in symmetrical sectorial divergence, while the stream of rarefactions, having the constraint of the symmetry removed, diverges through the sides of the cone from every surface and gives rise to the observed currents in the air outside the cone. In the case of suction or inward flow, on the other hand, it would appear that the conditions of symmetrical divergence of energy subsist in substance.

We shall return later to the interpretation of these results, and shall now proceed to the calculation of the "centre of phase" for cases of divergence supposed symmetrical. We shall base these calculations on the construction of a wave-front, in a manner somewhat analogous to the construction of Huyghens in optics; *i. e.* spheres with radius r are described from all points of the source-surface S_0, and the external envelope of these spheres is treated as the wave-front. This involves several hypotheses which are certainly not accurately fulfilled; at the same time it affords a sufficiently close approximation for many purposes to the state of things supposed in the theory of Helmholtz.

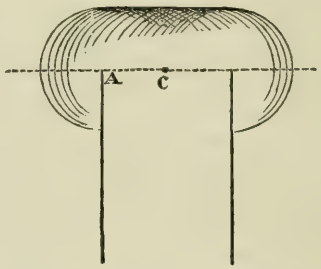
If in this case we suppose the disturbance uniformly distributed over each wave-front, we have general conditions resembling in their symmetry those of symmetrical spherical divergence. Under these circumstances we may assume that all the energy-elements are reflected back into the source S_0; and we easily obtain values for the centre of phase fairly agreeing

with the numerical results of Helmholtz's theory and with experiment. It must be understood that these numerical results can be obtained in several different ways; and other conditions, such as knowledge of the coefficient of extinction, or proportion of energy failing to reach the source after reflexion, and knowledge of the actual form of motion, must be applied to distinguish between the hypotheses. The calculation reduces itself, according to the methods of the last note, to the evaluation of

$$\int r\frac{dS}{S^2} = \bar{r}\int\frac{dS}{S^2},$$

where S is the surface of the wave-front.

To determine this surface, let a be the radius A C of the circular end (S_0) of a cylindrical tube, r the radius with which the spheres are described whose sections are the circles shown, r being also the distance through which a given disturbance is supposed to have travelled since it left S_0. It is required to find the surface of revolution about the axis of the tube traced out by the outer limit of the circles shown.



The curved half-ring surface traced out by the semicircle whose centre is A is easily found by the theorem of Guldin; it is

$$\pi r \times 2\pi\left(\frac{2r}{\pi} + a\right) = 4\pi r^2 + 2\pi^2 ar.$$

Adding to this the plate πa^2 which lies parallel to the circular end of the pipe, the whole surface is

$$4\pi r^2 + 2\pi^2 ar + \pi a^2.$$

Or, if we suppose the flange (indicated by the dotted lines at the sides) to be introduced, the curved part has half the value above stated, and the surface for the case of hemispherical divergence becomes

$$2\pi r^2 + \pi^2 ar + \pi a^2.$$

As all our proceedings are approximate, I shall not introduce the above expressions for the surface into the integrals, but employ functions of a simpler type, conditioned to have the value πa^2 at S_0, a value determined from the above at $r = a$, and a value approximating to that of sphere or hemisphere for large values of r.

First, then, when $r=a$, the above values give for S,

without flange ... $\pi a^2(5+2\pi)=11{\cdot}3\,\pi a^2$,

with flange ..... $\pi a^2(3+\pi) = 6{\cdot}1\,\pi a^2$.

The conditions are satisfied roughly by the following assumption for the case without flange,

$$S=\pi(a+2r)^2.$$

When r is great, this represents nearly a sphere of radius r. Making this substitution in the formula

$$\int_0^\infty r\frac{dS}{S^2}=\bar{r}\int_0^\infty\frac{dS}{S^2},$$

we find

$$\bar{r}={\cdot}50\,a.$$

We shall see that the experimental determinations lead us to a value of about $\cdot55\,a$; so that experiment is thus fairly represented.

The calculation of the case with flange may be derived from the above by assuming $S=\pi(a+\sqrt{2}\,r)^2$, which makes $S_a=5{\cdot}8\pi a^3$, the wave-front condition requiring $6{\cdot}1\,\pi a^2$ and $S_\infty=2\pi r^2$. Applying the above formula, we find

$$\bar{r}=\frac{a}{\sqrt{2}}={\cdot}707\,a.$$

The following is another form of assumption of a more elastic character, in which we employ a combination of two forms of surface having a common value at $r=a$. Consider first the hemispherical case (with flange). We can represent the wave-front surface ($6{\cdot}1\,\pi a^2$ when $r=a$) by

$$S=\pi(a^2+5r^2);$$

then, in order to make the surface tend to that of a hemisphere, we must alter the assumed form between $r=a$ and $r=\infty$ and put

$$S=\pi(4a^2+2r^2),$$

which tends to a hemisphere when r is great. For the purpose of this calculation the following formula is convenient:—

If

$$S_1=\pi(m_1^2a^2+n_1^2r^2),$$

$$S_2=\pi(m_2^2a^2+n_2^2r^2),$$

and

$$m_1^2+n_1^2=m_2^2+n_2^2,$$

then

$$\int_0^a r\frac{dS_1}{S_1^2}+\int_a^\infty r\frac{dS_2}{S^2}=\frac{1}{\pi a}\left(\frac{1}{m_1n_1}\tan^{-1}\frac{n_1}{m_1}+\frac{1}{m_2n_2}\left(\frac{\pi}{2}-\tan^{-1}\frac{n_2}{m_2}\right)\right).$$

In the above case,

$$m_1^2=1, \quad n_1^2=5,$$
$$m_2^2=4, \quad n_2^2=2.$$

Then equating the result of the above formula to $\frac{\bar{r}}{\pi a^2}$, we find $\bar{r}=\cdot 85\,a$, which is a little greater than the value ($\cdot 82\,a$) given by Lord Rayleigh.

The two values given by these two hypothetical forms of motion lie on opposite sides of the true value for hemispherical divergence; we may conclude therefore that the true form is intermediate in character between the two.

We may apply the above formula to get a more exact representation of the hypothetical complete divergence without flange. Here the surface when $r=a$ was to be $11\cdot 3\,\pi a^2$. We will put

$$m_1^2=1, \quad n_1^2=10,$$
$$m_2^2=7, \quad n_2^2=4,$$

making $S=11\,\pi a^2$; whence we find

$$\bar{r}=\cdot 574\,a,$$

which represents closely the experimental value I adopt ($\cdot 55\,a$).

That it may be understood clearly how it is that I do not consider the correspondence of the values of this theory with experiment to prove the hypothesis of uniform spreading, I proceed to point out that the conceivable forms of divergence are infinite in number, and that for every one a law of divergence of the reflected elements may be imagined which will give the results in question. To test whether any one form is the real one, it is necessary either to investigate the form by direct experiment (which is the course I have selected), or to determine experimentally the degree of resonance, or to produce a complete theory determining the point (which in my opinion cannot at present be done). Such a theory has first to account for the fact that air issuing under low pressure from the end of a tube diverges in a cone whose vertical angle is approximately 20°, and excites in the surrounding air streams of the nature which have been described. Without dealing generally with the infinitely various forms of divergence, I will touch upon certain cases which illustrate the passage from the one form to the other; and it will be convenient to associate these with the simplest forms which can be supposed to be assumed by the law regulating the divergence of the reflected elements of energy per second.

The divergence of the reflected elements could conceivably take place in several ways:—First, according to the law which

would subsist if we treated each reflected element as an independent source, and applied the Helmholtz-Rayleigh theorem of reciprocity. This simply amounts to saying that it does not matter which way a disturbance travels from one point to another; the fraction of the energy per second of unit surface at the source which reaches the unit receiving surface is the same, whichever of the two be source or receiver. In this case it is easy to see that the above fraction, from unit surface to unit surface, is $\left(\frac{S^0}{S}\right)^2$, if we suppose the divergent stream to behave as in spherical divergence. (For the fraction of energy from S_0 that reaches S is $\frac{S_0}{S}$; and of this only the fraction $\frac{S_0}{S}$ lies on the surface S_0 equal to that of the source.) The fraction of any energy-element from S that returns to S_0 is then measured by $\frac{S_0}{S}$. (For it is the fraction $\left(\frac{S_0}{S}\right)^2$ taken as many times as the surface S_0 goes into the surface S.) The energy reflected from surface S to S_0 is consequently proportional to $\frac{dS}{S^3}$, the reflected element itself being proportional to $\frac{dS}{S^3}$). This is on the hypothesis that the reflected element behaves as an independent source.

Secondly, it may be imagined that the energy-element diverges from the reflecting surface S in the same manner as if it were diverging from an image of the source S_0 placed behind S. The motion would be, from this point of view, regarded as a directed one, of the nature of projection of a number of small particles from S_0 which make their way by impacts. For small distances from S_0, the surface S, in which elements of energy emerging simultaneously in paths nearly parallel lie at any time, is approximately plane. The magnitude of the surface Σ in which they would lie after a formal reflexion at S, according to the ordinary law (angle of incidence = angle of reflexion), = the plane section of the cone of divergence lying at the same distance from S as S from S_0. Consequently

$$\frac{\Sigma}{S} = \frac{S}{S_0}, \text{ or } \Sigma = \frac{S^2}{S_0}.$$

This surface Σ, which should be occupied by the energy reflected from S, lies in the plane of S_0; and the fraction of reflected energy that would reenter S is

$$\frac{S}{\Sigma} \cdot \frac{S_0}{\Sigma} = \frac{S_0^2}{S^3}.$$

The reentering energy-element is here measured by $\frac{dS}{S^5}$.

Thirdly, it is tolerably clear that the conception of the last case is correct so far as the projection of the air goes, but not in regarding the reflexion as like that of particles. What really happens is, that the disturbance in its advance leaves a certain defect of pressure behind it as it expands; and this behaves likes a suction of air into a circular opening, the surrounding air pressing into it pretty uniformly from all directions. We shall return to this case.

First, then, according to the law of reciprocity, which treats the reflected impulse like an independent source, the element of energy which reaches S_0 from S is measured by $\frac{dS}{\overline{S}^3}$; consequently the "centre of phase" of the reflected vibration is determined by the equation

$$\int_{S_0}^{\infty} r\frac{dS}{\overline{S}^3} = \bar{r}\int_{S_0}^{\infty}\frac{dS}{\overline{S}^3} = \frac{\bar{r}}{2S_0^2}.$$

The following are the results for a few assumed forms under this law:—

S_0^a.	S_a^∞.	for law expressed by $\frac{dS}{\overline{S}^3}$. $\frac{\bar{r}}{a}$.
$\pi(a^2+r^2)$	$\pi(a^2+r^2)$	$\frac{\pi}{4}$
$\pi(a^2+r^2)$	$2\pi r^2$	·726
$\pi(a^2+r^2)$	$4\pi r^2-2\pi a^2$	·69
$\pi(a^2+2r^2)$	$\pi(a^2+2r^2)$	·555
$\pi(a^2+2r^2)$	$4\pi r^2-\pi a^2$	·53
$\pi(a^2+3r^2)$	$4\pi r^2$	·45

We see that this law, which we may call the reciprocity law for the moment, requires a form of motion somewhat different from any we have hitherto come across. The motion represented by the first entry, which gives the number of the Helmholtz theory, certainly does not exist; nor do really any of the others. Yet the results are useful; for these are functions of the type of those which must express the motion. We can draw at least one conclusion about such functions in general, for which we have been already prepared. Compare the cases in which the same form at $r=a$ diverges into hemisphere and sphere. One such pair of values is ·726, ·69; an-

other such pair is ·555, ·53. Hence we infer that a flange which imposes hemispherical divergence affects the numerical result by altering the form of motion near the source, and that the difference between the results of various forms at great distances is insignificant if the form near the source is constrained to be the same.

Secondly, according to the law of reflexion as from an image of the source,

$$\int_0^\infty r\frac{d\mathrm{S}}{\mathrm{S}^5} = \bar{r}\int_0^\infty \frac{d\mathrm{S}}{\mathrm{S}^5}$$

$$= \frac{\bar{r}}{4\mathrm{S}_0^4}.$$

We can determine an approximately conical form of expansion in this case which agrees fairly with the observed conditions, as far as the position of the centre of phase and angle of divergent cone are concerned; but the part of the observed phenomenon which consists of the flow of the surrounding air towards the diverging cone is not truly represented; and we have seen that the hypothesis, of which the law is an expression, is not admissible. Assume

$$\mathrm{S} = \pi(a+kr)^2,$$

which represents a plane circle of radius $a+kr$; this may be represented as tracing out a cone of semivertical angle k. If we then calculate $\bar{r}$ by the above formula, we find

$$\bar{r} = \frac{a}{7k}.$$

Ascribing the known values to $\bar{r}$, we find

$\bar{r}$.	$\tan^{-1}k$.
$\cdot 8a$	10° 8′
$\cdot 55a$	14° 35′ nearly,

which correspond to cones of about 20° and 29° vertical angle respectively. This corresponds fairly with experiment, and shows that we *are approximating to the form of function which is capable of representing the observed facts.*

Let us now turn to the state of things experimentally found in the case of outward flow. We shall, as above, put

$$\mathrm{S} = \pi(a+kr)^2;$$

but from S we shall suppose the reflected rarefaction to diverge in the manner represented by drawing spheres from the disturbed points as centres, and we consider the surface Σ thus covered after divergence through r. The wave-front on circle

of radius ρ at distance r is, as before,

$$2\pi r^2+\pi^2\rho r+\pi\rho^2\ ;$$

or putting $\rho=a+kr$,

$$\Sigma=\pi\{r^2(2+\pi k+k^3)+ar(\pi+2k)+a^2\}.$$

The element diminishes in divergence as the surface increases; and of that on Σ only $\frac{S_0}{\Sigma}$ reaches S_0; so that the total energy that reaches S_0 is measured by

$$\frac{dS}{S^2}\times\frac{S}{\Sigma}\times\frac{S_0}{\Sigma}=\frac{S_0\,dS}{S\Sigma^2}.$$

The surface Σ when $r=a$ has the value

$$\Sigma_a=\pi a^2(3+\pi(1+k)+2k+k^2).$$

Suppose k to be a small fraction, such that the term which involves it can be neglected for approximate purposes. We have then to represent the law of variation of the function $\frac{1}{S\Sigma^2}$ by a power of S, such that the two functions shall have the same value at $r=0$ and $r=a$; we neglect the difference at great distances.

Let $\Sigma=\frac{S^x}{S_0^{x-1}}$, where $r=a$; then $\Sigma=S_0$ when $r=0$.

When $r=a$,

$$\Sigma=(3+\pi)\pi a^2,\text{ approximately,}$$

neglecting terms in k; and

$$S=\pi(a+kr)^2;$$

$$\therefore\ 3+\pi=(1+k)^{2x},\text{ approximately;}$$

$$\therefore\ \cdot788=2x\mathrm{M}k,$$

where $\mathrm{M}=\cdot434$ (modulus of logarithms).

$$\therefore\ kx=\cdot9,\text{ nearly.}$$

In the equation

$$\int_0^\infty r\frac{dS}{S\Sigma^2}=\bar{r}\int_0^\infty\frac{dS}{S\Sigma^2}.$$

Putting $\Sigma=\frac{S^x}{S_0^{x-1}}$, we get

$$\int_0^\infty r\frac{dS}{S^{2x+1}}=\bar{r}\int_0^\infty\frac{dS}{S^{2x+1}};$$

whence, since $S=\pi(a+kr)^2$,

$$\bar{r}=\frac{a}{k(4x-1)},\text{ and }kx=\cdot9;$$

$$\therefore\ \bar{r}=\frac{a}{3\cdot6-k}.$$

That is, for small values of k, $\bar{r}$ approximates to a value of about $\cdot 3a$ under the circumstances of motion under investigation.

In the present unsettled condition of the experimental values for tubes which are very long in proportion to their diameter, it would be rash to pronounce definitively; but, so far as I know, values of r so low as this are not well established, although, as far as my own experiments go, I cannot say that $\cdot 3a$ is beyond the range of experimental error. If for the present, however, we admit that the value $\cdot 55a$ represents the present experimental results more nearly, we learn that the divergence of the reflected stream of energy, so far as it lies within the issuing stream of air, does not take place in the manner above supposed, *i. e.* it does not spread freely with hemispherical divergence, but behaves more, as far as amount of divergence goes, so as to agree with the law of reflexion from an image of the source. The analytical discussion of the actual motion is a matter which I do not propose to attempt; but the following considerations will show the general nature of the motion regarded as a modification of spherical divergence, and will give some idea of the extreme complexity of this part of the problem.

In spherical or sectorial divergence we saw that the reflected energy formed a convergent stream, and suggested that divergence might be prevented by the symmetry (*i. e.* all the motions necessary for divergence may be reduced to equal pairs in opposite directions). In the present case of divergence through a cone of small vertical angle, the constraint at the exterior surface of the cone is entirely removed, the reflected energy close to the surface diverges freely in the hemispherical form, and gives rise to the inward flow towards the surface of the cone which takes place through the surrounding air. But in positions near the axis of the issuing cone there is but little, if any, less constraint than in the case where the sectorial form is maintained by enclosure within walls; so that this portion of the reflected stream does not get away freely, as is supposed in the last investigation.

The results up to the present point are shortly as follows:—

Referring the case of sound issuing from a tube to the case of continuous flow instead of the case of electricity, when the wave-length becomes great with respect to all the dimensions, we get a case which we can study experimentally.

The experimental study teaches us that the form of velocity-potential derived from the hypothesis of a tendency to uniform spreading does not represent the form of divergence for outward flow, but that it does represent the form of divergence for inward flow.

We then showed how to calculate approximately the position of centre of phase for the case of uniform spreading from the end of a pipe both with and without flange.

We then showed that there are an infinite number of possible forms of divergence, which can satisfy the known numerical conditions on the assumption of a suitable law of divergence of reflected elements, and came to the conclusion that the reflected energy-elements diverge within the issuing cone nearly according to the numerical law which would hold if they were reflected as if issuing from an image of the source. We see that the real explanation cannot involve any such reflexion ; and we get a sort of idea of the direction in which the explanation lies.

[To be continued.]

Erratum in Note 5 (p. 30, July).

The variable terms in the density for (i) and (ii) should read,

$$\text{(i)} \quad -\frac{\mathrm{DC}}{r^2}\frac{kr}{v}\cos k(vt-r),$$

$$\text{(ii)} \quad -\frac{\mathrm{DC}}{r^2}\frac{kr}{v}\cos k(vt+r).$$

(The r^2 in the denominators was omitted in copying.)

XVIII. *On a Generalization of* Taylor's *Theorem.* *By* J. J. Sylvester*.

CONNECTED with the study of the Theory of the symmetrical functions of the differences of the roots of an Algebraical Equation, a theorem presents itself in Dr. Salmon's 'Lessons on Higher Algebra,' 3rd edition, p. 59, art. 63, only partially indicated and insufficiently demonstrated there, which on a closer inspection will be found to be well deserving of notice as containing a true generalization of Taylor's theorem, leading to a development of the same form, subject to a like law of convergence, and easily demonstrable by the same method as that theorem.

Let f be *any function whatever* of $a, b, c, \ldots$, and f_1 the same function of $a_1, b_1, c_1, \ldots$, where

$$a_1 = a, \quad b_1 = b + ah, \quad c_1 = c + 2bh + ah^2,$$
$$d_1 = d + 3ch + 3bh^3 + ah^2, \ldots$$

and let Ω represent the operator

$$a\frac{d}{db} + 2b\frac{d}{dc} + 3c\frac{d}{d.d} + \ldots ;$$

* Communicated by the Author.

then the theorem in question affirms that

$$f_1 = f + \Omega . fh + (\Omega .)^2 f \frac{h^2}{1.2} + (\Omega .)^3 f \frac{h^3}{1.2.3} + \ldots .$$

On making $a=1$, $b=x$, $c=0$, $d=0 \ldots$, the theorem becomes Taylor's. To prove it in its general form, let

$$\phi x = ax^n + nbx^{n-1} + n\frac{n-1}{2} cx^{n-2} + \ldots ;$$

then, on substituting $x+h$ for x, ϕx becomes

$$= a_1 x^n + nb_1 x^{n-1} + n\frac{n-1}{2} c_1 x^{n-2} + \ldots .$$

Let h become $h+\delta h$, then obviously

$$\delta f_1 = \frac{d}{dh} f_1 \delta h.$$

But we may obtain the new values of $a_1, b_1, c_1, \ldots$ corresponding to the change of h into $h+\delta h$, by substituting in ϕx first $x+\delta h$ and then $x+h$ for x.

The effect of the first substitution is to change $a, b, c, \ldots$ into $a+\delta a, b+\delta b, c+\delta c, \ldots$, where

$$\delta a = 0, \quad \delta b = a\delta h, \quad \delta c = 2b\delta h, \quad \delta d = 3c\delta h, \ldots .$$

Hence the increment

$$\delta f_1 = \left(a\frac{d}{db} + 2b\frac{d}{dc} + 3c\frac{d}{d.d} \ldots \right) f_1 . \delta h ;$$

consequently

$$\frac{d}{dh} f_1 = \Omega . f_1 .^*$$

Hence, if we write

$$f_1 = f + Bh + Ch^2 + Dh^3 + \ldots ,$$

we shall have

$$B + 2Ch + 3Dh^2 + \ldots$$
$$= \Omega f + \Omega Bh + 2\Omega Ch^2 + \ldots .$$

Hence

$$B = \Omega . f, \; C = \tfrac{1}{2}(\Omega .)^2 f, \; D = \frac{1}{2.3}(\Omega .) f^3 \ldots ;$$

* Or without introducing ϕx, the equations between $a_1, b_1, c_1 \ldots$ and $a, b, c, \ldots$ show by direct inspection that the effect upon the former is the same, whether we augment h by δh or $b, c, d \ldots$ respectively and simultaneously by $a\delta h, 2b\delta h, 3c\delta h, \ldots$ so that $\frac{d}{dh} f_1 = \Omega f_1$, as in the text.

and consequently

$$f_1 = f + \Omega . f + (\Omega .)^2 f \frac{h^2}{1.2} + (\Omega .)^3 f \frac{h^3}{1.2.3} + \ldots,$$*

and the first part of the theorem is demonstrated. It will of course be understood that $(\Omega .)^i$ means not $(\Omega^i) .$, but $\Omega . \Omega . \Omega .$ (to i factors).

Lagrange's or any other rule for the Remainder in the old Taylor's theorem may be extended to this generalization of it; that is to say, if in the development of f_1 we stop at the nth term, the *remainder* will be equal to

$$\frac{h^n}{\Pi n} (\Omega .)^n f(\alpha, \beta, \gamma \ldots),$$

where $\alpha, \beta, \gamma \ldots$ are what $a_1, b_1, c_1 \ldots$ become when we write θh for h, θ being some proper positive fraction. The demonstration proceeds *pari passu* for the generalized form and for Taylor's case of it. Thus, consider Bertrand's proof as given in Williamson's 'Calculus,' second edition, p. 64.

The *lemma* upon which the proof depends takes the form, that if f_1 (supposed continuous between two values of h) has the same value (zero, as it happens in the matter in hand) for two values of h, Ωf must vanish for some intermediate value of h; which is obviously true, since $\delta f = \Omega f \delta h$. The rest of the demonstration remains essentially the same, *mutatis mutandis*, at each point as for Taylor's theorem properly so called.

The theorem above established easily admits of extension to the case of $a_1, b_1, c_1 \ldots$ being the values assumed by $a, b, c \ldots$, when in the quantic $(a, b, c \ldots)(x, y, z)^n$ we substitute $x + hy + kz + \ldots$ for x. We may thus obtain a theorem which will bear to Taylor's theorem for any number of variables the same relation as the theorem given in the text to Taylor's theorem for a single variable.

Since the effect of changing x into $x + h + \delta h$ may be obtained either by first substituting $x + h$ for x and then $x + \delta h$ for x in ϕx, or by a reversal of the order of these two processes, we obtain the interesting consequence that the two operators

$$a \frac{d}{db} + 2b \frac{d}{dc} + 3c \frac{d}{d.d} + \ldots$$

and

$$a_1 \frac{d}{db_1} + 2b_1 \frac{d}{dc_1} + 3c_1 \frac{d}{d.d_1} + \ldots$$

* Consequently, if Ωf vanishes, since also $(\Omega .)^i f$ will also vanish for all values of i, we shall have $f_1 = f$. It is this fact of $(\Omega f = 0)$ being the complete solution of $(f_1 = f)$ which constitutes the importance of the theorem in the Calculus of Invariants.

are absolutely identical,—a theorem which of course admits, but not without a somewhat complicated process, of an *à posteriori* direct proof; so that the operator Ω is to all intents and purposes what Professor Cayley calls a semi-invariant or pene-invariant, but to which I am accustomed to give the name of a *differentiant* to ϕx.

Finally, it may be observed that a development for f_1 may be obtained by the use of the ordinary Taylor's theorem for *several* variables. If we make use of this method, and write in addition to

$$\Omega = a\frac{d}{db} + 2b\frac{d}{dc} + 3c\frac{d}{d\,.\,d} + \ldots,$$

$$\Omega_1 = a\frac{d}{dc} + 3b\frac{d}{d\,.\,d} + 6\frac{d}{d\,.\,e} + \ldots,$$

$$\Omega_2 = a\frac{d}{d\,.\,d} + 4b\frac{d}{d\,.\,e} + 10\frac{d}{d\,.\,f} + \ldots,$$

&c. = &c.,

we shall obtain the noteworthy symbolical and absolute identity

$$e^{h\Omega\,.} = e^{h\Omega + h^2\Omega_1 + h^3\Omega_2 + \ldots}\,*,$$

which may be verified, but not without some little trouble, by direct expansion.

If we use $\Omega\,!$ to signify that Ω is to be used as a pure operator on the matter coming after it (operating that is to say

* If we write

$$\Delta = (-\Omega\,.\,+\Omega)h + \Omega_1 h^2 + \Omega_2 h^3 + \ldots,$$

we ought to have $e^{\Delta} - 1 = 0$, and the coefficients in the expansion of $e^{\Delta} - 1$ according to ascending powers of h ought all to vanish identically; and so they will be found to do, provided that in each such coefficient expressed as the sum of the product of powers of Ω_0, Ω_1, Ω_2, ... and of $\Omega\,.$ the power of the *dotted* Ω be taken last in order. As soon as that expansion is made (but of course not before) we may write $\Omega\,.\,-\Omega = 0$, and we may readily calculate *à priori* the value of each power of $(\Omega\,.\,-\Omega)$; thus we shall obtain

$$(\Omega\,.\,-\Omega)^2 = \Omega\,.^2 - 2\Omega\Omega\,.\,+\Omega^2 = \Omega\,.^2 - 2\Omega^2 + \Omega^2 = 2\Omega_1;$$

and so by a similar calculation, having first determined $\Omega\,.^2$, $\Omega\,.^3$, $\Omega\,.^4$, &c., we shall obtain

$$(\Omega\,.\,-\Omega)^3 = 6\Omega_2, \quad (\Omega\,.\,-\Omega)^4 = 24\Omega_3 + 12\Omega_1{}^2, \text{ \&c.};$$

on substituting these values in $\Delta + \frac{\Delta^2}{1\,.\,2} + \frac{\Delta^3}{1\,.\,2\,.\,3} + \ldots$ the coefficients of the several powers of h will be found to vanish.

The appearance in the above process of a zero whose powers are not zero is a phenomenon which will not shock those who are acquainted with Professor Peirce's discussions of possible algebras; but it is new to find it occur in working out a symbolical identity.

solely on the symbols of quantity $a, b, c, \ldots$ and not on the operators $\frac{d}{da}, \frac{d}{db}, \frac{d}{dc} \ldots$), we shall have

$$\Omega_1 = \frac{(\Omega\,!\,\Omega)}{1.2}, \quad \Omega_2 = \frac{(\Omega\,!\,\Omega\,!\,\Omega)}{1.2.3},$$

and so on. Hence the "noteworthy" symbolical equation above written may be put under the hypersymbolical form

$$e^{h\Omega}\bullet = e^{(e^{h\Omega\,!}-1)\frac{\Omega}{\Omega\,!}}$$

a suggestive identity that may possibly call forth a sneer from the mathematical cynic, but not from the thoughtful mathematician, who, aware that algebra is in its essence a language which it is the proper business of his art to fathom and develop, is prompt to recognize every step in expression as a gain in power.

The theorem $f_1 = e^{h\Omega}\bullet f$ having, as far as I am aware, been first given by Dr. Salmon in a form, if not quite complete, still sufficient for the immediate purpose to which it was to be applied, ought, I think, in justice to bear his name; and I see no reason why Salmon's Theorem in its totality should not be expected in the future to bear new fruit in algebraical expansions and other uses as important as have flowed from the one familiar and simplest case of it, known as Taylor's Theorem. Thus, *ex. gr.*, for the special case where f_1 becomes a function of one only of the quantities $b_1, c_1, \ldots$ the Salmonian theorem reproduces Arbogast's celebrated one for expanding a rational integral function by the method of derivations, but under a greatly improved form of notation, and with the advantage of a test of convergency supplied by the *limit to the remainder* given in the text above. Who on a first casual reading could have imagined that Arbogast's problem in the differential calculus was virtually solved in an improved form in an article treating "on the symmetrical functions of the differences of the roots of an equation"? "*Que diable allait-il faire dans cette galère là!*" may rise to the lips of many a reader on being made acquainted with the fact*.

Johns Hopkins University, Baltimore,
May 29, 1877.

* Using Q to denote any rational integral function of x, Salmon's theorem is a theorem for expanding any function of Q, $\frac{dQ}{dx}, \frac{d^2Q}{dx^2}, \ldots$ in terms of ascending powers of x.

XIX. *Proceedings of Learned Societies.*

ROYAL SOCIETY.

[Continued from p. 73.]

January 18, 1877.—Dr. J. Dalton Hooker, C.B., President, in the Chair.

THE following paper was read:—

"Residual Charge of the Leyden Jar.—II. Dielectric Properties of various Glasses." By J. Hopkinson, M.A., D.Sc.

I. The two following propositions are included under the law that the effects of simultaneous electromotive forces are superposable.

(*a*) If two jars be made of the same glass but of different thicknesses, if they be charged to the same potential for equal times, discharged for equal times, and then insulated, the residual charge will after equal times have the same potential in each.

(*b*) Residual charge is proportional to exciting charge.

These propositions are verified experimentally within the limits of errors of observation.

II. Electric displacement through a dielectric may be supposed to depend not only on the electromotive force at the instant, but also in part on the electromotive forces at all previous times. If we assume that the effect of the electromotive force at any previous time decreases according to some law as the time elapsed increases, and that these effects are superposable, we may write

$$y_t = x_t + \int_0^\infty x_{t-\omega}\psi(\omega)d\omega,$$

where x_t is the electromotive force at time t, and y_t is the surface integral of electric displacement divided by the instantaneous capacity of the jar.

If $\psi(\omega)$ is determined for all values of ω, the properties of the glass as regards conduction and residual charge are completely expressed.

$\psi(\infty)$ is equal to the reciprocal of the specific resistance of the material multiplied by 4π and divided by the specific inductive capacity. During insulation y_t is constant; hence

$$x_t = \mathrm{A} - \int_0^\infty x_{t-\omega}\psi(\omega)d\omega.$$

This is the fundamental equation of the following experiments.

Two methods of finding values of $\psi(\omega)$ present themselves.

1st. Let x_t be constant $= \mathrm{X}$ for a time T; insulate for time t.

$$x_t = \mathrm{A} - \int_0^{t+\mathrm{T}} x_{t-\omega}\psi(\omega)d\omega;$$

$$\frac{dx_t}{dt} = -\mathrm{X}\,\psi(t+\mathrm{T}) - \int_0^\infty \frac{dx_{t-\omega}}{dt}\psi\,\omega d\omega.$$

If t be small,

$$\frac{dx_t}{dt} = -\,\mathrm{X}\psi(\mathrm{T}),$$

and the value of $\frac{dx_t}{dt}$ may be observed with more or less accuracy.

2nd. Let x_t be constant = X for a very long time T previous to time $t=0$; discharge and at time t insulate and observe $\frac{dx_t}{dt}$.

$$x_t = \mathrm{A} - \mathrm{X}\int_t^{\mathrm{T}+t} \psi(\omega)d\omega\,;$$

$$\frac{dx_t}{dt} = \mathrm{X}\left\{\psi(t) - \mathrm{B}\right\}.$$

There are also methods of verification. For example, charge during time T′, reverse the charge for time T″ and discharge; then after time t insulate and observe $\frac{dx_t}{dt}$; we shall find

$$\frac{dx_t}{dt} = \mathrm{X}\left\{\psi(t) - 2\psi(\mathrm{T}'' + t) + \psi(\mathrm{T}'' + \mathrm{T}' + t)\right\}.$$

III. Experiments were tried on ten glasses. The verifications were perhaps as close as could be expected, considering that no attempt was made to observe at a constant temperature. The glasses were :—

No. 1. A soda-lime glass containing much soda.
No. 2. A soda-lime glass coloured deep blue with oxide of cobalt.
No. 3. Window-glass.
No. 4. Optical hard crown.
No. 5. Soft crown.
No. 6. A very light flint glass.
No. 7. Light flint.
No. 8. Dense flint.
No. 9. Extra-dense flint.
No. 10. Opal glass.

Glasses 1, 2, and 3 agree in possessing high conductivity and also large values of $\psi t - \mathrm{B}$; whilst 7, 8, 9, 10 have a high resistance (thousands of times as great as 1, 2, or 3) and small residual charge.

IV. Electrolytic conduction may occur through the soda-lime glasses at the ordinary temperature of the air.

Summary.—The experiments appear to verify the fundamental hypothesis, viz. that the effects on a dielectric of past and present electromotive forces are superposable. Ohm's law asserts the principle of superposition in bodies in which conduction is not complicated by residual charge. Conduction and residual charge may be treated as parts of the same phenomenon—an after effect, as regards electric displacement, of electromotive force. The experiments appear to show that the principle of Ohm's law is true of the whole phenomenon of conduction through glass.

March 8.—Dr. J. Dalton Hooker, C.B., President, in the Chair.

The following paper was read:—

"On Magneto-electric Induction in Liquids and Gases.—Part I. Production of Induced Currents in Electrolytes." By J. A. Fleming, B.Sc. (Lond.).

This paper contains an account of an experimental inquiry into the production of induced currents in liquids by magneto-electric induction. Faraday examined one such case of induction, in which a conducting liquid was used as a secondary circuit. He coiled round the armature of an electromagnet an india-rubber tube filled with dilute sulphuric acid, and found, on making and breaking the primary circuit, the induced currents generated in it, as in the case of metallic conductors; but he could not obtain any effect when brine, sulphuric acid, or other solutions were rotated in basins over a magnet, or enclosed in tubes and passed between the poles. He failed also to detect any magneto-electric current in water flowing across the earth's lines of magnetic force (viz. in the river Thames).

Since the reason for these negative results is not at once obvious, it seemed desirable to repeat and extend them to other cases, so that, if possible, the analogy of electrolytic with solid conductors might, in respect to magneto-electric induction, be completed. In addition, the subject involves the interesting question of the magneto-electric phenomena accompanying the flow of ocean-currents and other large masses of water.

Three cases of induction in liquids flowing in a magnetic field or traversed by lines of magnetic force have been examined.

1. *Production of induced current in a liquid stream flowing uniformly in a constant magnetic field.*—When a stream of conducting fluid flows vertically down between the poles of a magnet a transverse current is produced in a direction at right angles to the lines of force and line of flow. This was obtained in the following way:—A glass tube, about 200 centims. long and 2 centims. wide, had platinum plates 15 millims. wide placed along its inside and at opposite sides, with their lengths parallel to the axis of the tube. Platinum wires welded to these plates were sealed through the glass. The plates were curved to lie closely against the sides of the tube. This tube was placed vertically between the poles of a large electromagnet, the line joining the platinum plates being at right angles to the line of the poles.

To the upper end of the tube was attached another, leading to a reservoir of dilute sulphuric acid placed high above the floor; to the lower end a tube leading to a receptacle on the floor. The platinum plates were then connected with a distant galvanometer. When the magnet was not excited, no flowing of the liquid had any effect on the galvanometer; but when it was excited, at the moment the flow began the galvanometer showed a deflection of 10° to 15°. Since the only part of the galvanometer circuit in motion is the liquid, this deflection was due to the magneto-electric

current generated in it by its movement. It was noticed that the plates were *polarized* by the currents so created. As a consequence of this, the deflection of the needle soon fell to zero; and on the liquid flow being stopped, a polarization current in the opposite direction was obtained. This proved that in experiments on induction in liquids, in order to obtain any constant current, non-polarizable electrodes must be used.

2. *Production of induced current in a mass of liquid rotating over a magnetic pole.*—In this case radial currents should be produced. They were obtained as follows:—Flat porous cells were placed round the circumference of a large basin, and in the centre a cylindrical one. These were filled with a solution of cupric sulphate, and contained copper plates. The basin was filled with dilute sulphuric acid. The centre copper plate was connected with one pole of the galvanometer, and the circumferential ones with the other. The whole was placed over the pole of the electromagnet. On exciting the magnet and rotating the dilute acid, a constant current was obtained, flowing from centre to circumference or the reverse according to the direction of rotation. With platinum electrodes the effect cannot be obtained, but with non-polarizable electrodes it is easily produced. Mercury was likewise tried with still better results.

3. *Production of induced current in a liquid at rest in a variable magnetic field.*—If a flexible tube filled with conducting liquid is wound round an electromagnet, and into the ends electrodes placed so as to include a galvanometer in the circuit, then induced currents are obtained whenever the strength of the magnet varies. This is the case examined by Faraday. His experiment was repeated by MM. Logeman and Van Breda (Phil. Mag. [IV.] vol. viii. p. 465), who noticed that the electrodes were left polarized after the induced current had passed. These experiments were repeated with more powerful apparatus, using a soft-iron wire core within the inducing helix instead of solid iron, and employing a condenser in the primary circuit. Very strong induced currents were obtained, and correspondingly great polarization of the electrodes placed in the ends of the coil of acid. It was hoped that the currents might produce visible inductive electrolysis; but even this improved arrangement did not yield that result. Other saline solutions were tried with similar results.

Lastly, the phenomenon observed by Arago, of the retardation in the vibrations of a magnetic needle oscillated near the surface of liquids, is examined. Evidence is brought forward to show that this is *not*, as in the case of solid plates, due to induced currents created in the liquid:—(1) because the retardation is, *cæteris paribus*, not proportional to the conductivity of the liquid but dependent on its volatility; (2) because it takes place equally when a light brass needle, oscillated by torsion, is substituted for the magnet, provided the needle is light and the period of oscillation not very small. Thus a magnetic needle which required 4 min. 20 sec. to suffer a decrement of 25° in the semi-arc of vibration when in

air, required over dilute sulphuric acid 3 min. 30 sec., over ether 2 min. 25 sec. A brass needle of the same dimensions exhibited similar effects.

In conclusion the magneto-electric induction taking place in moving masses of water on the earth's surface under the influence of terrestrial magnetism is briefly discussed.

Before the introduction of the absolute system of electromagnetic measure, there was no means of estimating the electromotive force so brought into play by the flow of a river or ocean-stream, and the magnitude of the effect was perhaps overestimated.

A Table is given, showing the electromotive force in volts produced in two or three cases:—

	Difference of potential between two sides in volts.
Gulf-stream at lat. 30° N., long. 60° W.	8·6
Equatorial current, lat. 10° N., long. 40° W. ..	10·0
Dover and Calais tidal current	3·0
Thames at Waterloo Bridge	·016

This electromotive force without doubt generates a current transverse to the direction of the flow; but since the surrounding still water or the river-bed or channel is not a non-conductor, any attempt practically to detect it by plates placed on either side of the stream is not likely to succeed, since the current through the galvanometer is only a derived portion of the current in the stream.

A comparison of a chart of ocean-currents with one of the isogonic lines does not seem to show any distortion of the lines of equal variation where they cut across. If, now, electric currents of any great magnitude were generated in ocean-currents, such would undoubtedly be the case. Though Faraday's failure to detect any magneto-electric current in the Thames may have been partly due to his employment of polarizable electrodes, still there is evidence enough to show that these currents, though certainly existing and capable of being produced on a laboratory scale, cannot be regarded as contributing in any sensible degree towards affecting the form and distribution of the isogonic lines. Those who have looked to this as a possible partial cause of the irregularity observed have been led, no doubt, by the dimensions of the streams to exaggerate the magneto-electric induction caused by their flow.

March 15.—Dr. J. Dalton Hooker, C.B., President, in the Chair.

The following paper was read:—

"On the Density of Solid Mercury." By Prof. J. W. Mallet, University of Virginia.

I have lately taken advantage of a heavy fall of very cold and finely pulverulent snow, well adapted to the preparation of freezing-mixtures, to redetermine (with accuracy, I believe) the density of mercury in the solid state and at a definite temperature.

Such redetermination was not superfluous, as appeared from a collation of the statements to be found in various standard works. In the tables of specific gravities compiled by Prof. F. W. Clarke, and published by the Smithsonian Institution*, there are four authorities quoted, with the numbers given by these, as follows:—

	Sp. gr. of solid mercury.
Schulze	14·391
Biddle	14·485† at −60° C.
Kupffer and Cavallo	14 (approx.)
Joule	15·19

The last of these numbers, on reference to the original paper‡, turns out to represent no actual experiment with mercury itself, but is the density *calculated* for this metal from the examination of a number of amalgams. Kupffer and Cavallo do not profess to give the exact density, but merely state it as about 14, the number apparently resting on no special experiment, though I have not been able to verify this by reference to their paper§. The only other apparently independent statement I have met with occurs in the 'Annuaire du Bureau des Longitudes' for 1876 (p. 385), where the density 14·39 is given on the authority of Rivot; but I have not been able to find any reference to a paper by him bearing on this or any analogous point, and it seems probable that we have here only a reproduction of Schulze's result. In different handbooks of chemistry and physics numbers between 14 and 15 are given as approximations, but with no other authority than some of the above. Some of the best and most recent works simply state that mercury undergoes considerable contraction in freezing. Hence our knowledge on this subject appears hitherto to have rested on the experiments of Schulze and Biddle, both of which date back to the early years of the present century. Schulze's paper was published in 'Gehlen's Journal,' vol. iv. p. 434, and therefore about 1807 or 1808; and Biddle's‖ belongs to the year 1805. I have had access to neither; but the character of the instrumental means (balances, thermometers, &c.) generally available at the time the experiments were made, and the then imperfect knowledge of the constants needed for corrections to be applied, make it unlikely that very exact results could have been obtained. Biddle alone seems to have noted the temperature of the frozen mercury, and Brande¶ expresses doubt that this was determined with much accuracy. The temperature −60° C., if correctly quoted, is in itself somewhat improbable.

* "The Constants of Nature.—Part I." Smithsonian Miscell. Coll. 255, Washington, 1873, p. 24.

† 14·465 as quoted by Brande in his 'Manual of Chemistry.'

‡ Chem. Soc. Journ. [2] i. p. 387.

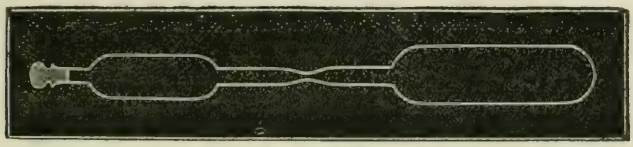
§ Quoted at second hand from Playfair and Joule, "On Atomic Volume and Specific Gravity," Chem. Soc. Mem. 2 (1845), p. 401, and 3 (1848), p. 57.

‖ Nicholson's Journal, vol. x. p. 253, and Tilloch's Philos. Mag. vol. xxx. p. 137.

¶ Manual of Chemistry, vol. i. p. 970.

The method adopted in the experiments lately made in this laboratory was the following:—

(1) A specific-gravity flask was prepared from a large cylindrical pipette, by closing in, and smoothly rounding, in the flame of the lamp one end of the cylinder, while the tube remaining attached to the other end was cut short and united by fusion to a second pipette of like shape but smaller size, the upper and open end of the shortened tube of which was fitted with a small carefully ground glass stopper. The neck between the larger and smaller cylinders was drawn down to a small bore (about 2 millims.), and at this narrowed part a fine line marked round it with a diamond. The shape of the vessel is shown in the annexed sketch, on a linear scale of one half the real size. The principal cylinder held about 58 cubic centimetres, and the small reservoir above 25 cub. centims. The whole vessel weighed about 46 grammes.



It enabled the experiments to be carried out with more than half a kilogramme of frozen mercury.

(2) This vessel having been accurately weighed when empty and dry, its capacity up to the mark was ascertained by filling it to this point with pure water at exactly 4° C., keeping it immersed for some time in a large mass of water at this temperature before making the final adjustment to the mark, wiping the outside dry, allowing the whole to acquire the temperature of the balance-case, and carefully weighing. The result of this direct calibration, deducting the weight of the vessel, was 59·7323 grammes or cubic centimetres at 4°.

(3) It was checked by emptying and drying the vessel, filling it to the mark with pure mercury at 0° C., the temperature being secured by keeping the whole surrounded by melting ice long enough to obtain perfect steadiness of position of the mercury, and weighing after the temperature of the balance-case had been regained. The mercury weighed 811·9997 grammes.

(4) The vessel was now surrounded by steam, and the mercury again brought to the mark, the temperature actually attained being 99°·5 C. (corrected for pressure). Allowed to cool down to the temperature of the balance-case, and again weighed, the mercury was found =799·7032 grammes. From the last two weighings the coefficient of cubical expansion for 1° C. of the glass used was, by the usual formula (taking absolute expansion of mercury from 0° to 100 = ·018153, as determined by Regnault), found = ·000027346.

(5) If now the density of mercury at 0° as referred to water at 4° be taken at 13·596 (Regnault), the weighing obtained in (3) gives the capacity of the vessel up to the mark at 0° =59·7234

cub. centims., or, applying the above coefficient of expansion of glass, 59·7300 cub. centims. at 4°. The mean of this value and that obtained in (2), $= \frac{59{\cdot}7300 + 59{\cdot}7323}{2} = 59{\cdot}7311$ cub. centims., was taken to represent the true capacity of the vessel at 4°.

(6) The freezing-mixtures used were prepared by cooling commercial hydrochloric acid (sp. gr. =1140) in the snow out of doors, the temperature of which, as well as of the air, was on the first day about −9° C., but on subsequent days rose to about −5°, mixing equal weights of this cooled acid and of snow, using separate portions of this first mixture to cool more acid and snow, and finally bringing together these last.

It soon appeared that little advantage was gained by trying to cool the snow, on account of its very low conducting-power in such a loose porous condition; and in the later experiments the temperature of the acid alone was lowered before the final mixture with snow. The glass vessels containing the mixtures were large enough to maintain the cold required for a long time, and steadiness of temperature was secured by surrounding them on all sides with a layer of cotton wadding, kept in place by stiff brown paper, and by conducting all the operations out of doors in the unusually cold atmosphere prevailing at the time.

(7) In determining the temperature of the freezing-mixtures an alcohol thermometer was used, graduated to single degrees, and admitting of half a degree being read; but the scale being found by no means accurate, its absolute readings were altogether discarded. By comparison with a good mercurial thermometer at three or four points between −10° and +40° C., and calculation from Is. Pierre's coefficients, the real length of a degree on the part of the stem corresponding to −40° was determined; and the temperature of fusion of the mercury being accurately noted and assumed =−38°·85 C., as determined by Balfour Stewart*, the addition or subtraction of four or five degrees, as above obtained, gave all the other temperatures observed.

(8) The above weighings and all others to be mentioned were made with an excellent balance by Becker, carefully adjusted and tested at the outset. With a load of a kilogramme in each pan a difference of weight of $\frac{1}{10}$ milligramme can be detected, and $\frac{1}{5}$ milligramme may be fully relied upon. All weighings were reduced by calculation to the corresponding results *in vacuo*, the temperature and pressure of the atmosphere being noted on each occasion; and the results quoted are those thus corrected.

(9) The specific-gravity flask was now filled with alcohol (at one time absolute, but which, by long keeping in the laboratory and occasional opening of the bottle, had absorbed some moisture, and was really about 95 or 96 per cent.), and three weighings were obtained after the liquid had been carefully adjusted to the mark at temperatures close to the freezing-point of mercury†.

* With an air-thermometer (Proc. Roy. Soc. 1863, vol. xii. p. 674).

† The alcohol, as afterwards mercury, was brought to near the required

Applying the correction for capacity of vessel at the respective temperatures, the three results were:—

cub. centims.			grms.
59·6625	of alcohol at	−37° C.	=50·7010
59·6600	„ „	−40°	=50·8316*
59·6576	„ „	−42°·5	=50·9092

or, reducing to one common weight,

cub. centims.			grms.
117·6752	of alcohol at	−37°	=100
117·3679	„ „	−40°	=100
117·1843	„ „	−42°·5	=100

(10) Taking the difference between (*a*) the first and second, (*b*) the second and third, and (*c*) the first and third of these numbers, and dividing each difference by the number of degrees in the interval of temperature, we get as the change of volume of 100 grammes of alcohol for 1° C.:—

	cub. centim.
From (*a*)	·1024
(*b*)	·0734
(*c*)	·0893

and the mean of these (·0884) may be taken to represent the coefficient for 1° C. within a range of a few degrees either side of the freezing-point of mercury. Using this coefficient to reduce the three weighings to their corresponding values for the same temperature, say −39° C., we have

grms.					cub. centims.
100	of the alcohol in question	at	−39°		=117·4984
„	„	„	„	„	=117·4563
„	„	„	„	„	=117·4937

the mean of which is 117·4828 cub. centims.

(11) The specific-gravity flask having been emptied and dried, 558·9353 grammes of mercury was introduced, the metal having just previously been purified by careful treatment with dilute nitric acid, washing with water, and quiet distillation from a glass retort. Filling up with the same alcohol as that used in the above experiments, and which had been kept in a well-stoppered bottle, the flask was gradually cooled, and finally, in the last freezing-mixture, the mercury frozen, and the alcohol brought exactly to the mark, taking care that it became and remained quite stationary, while during the freezing of the mercury the change of volume was very rapid and easily observable. The temperature having been noted when the final adjustment was made, the little flask was set aside, stoppered, until it could be washed off and dried, and was then allowed to acquire the temperature of the balance-case, and weighed.

temperature before introduction into the final freezing-mixture, and a separate small portion in a tube was similarly cooled, to be used in filling up to the mark if necessary. The stopper was carefully inserted as soon as the adjustment of the liquid was secured, so as to avoid any loss by evaporation.

* This weighing was not quite so satisfactory as the remainder; the temperature a little doubtful.

Three such experiments gave, aside from the weight of the flask itself,

		grms.
A.	Mercury + alcohol at $-39°$ C.	$=576·2029$
B.	„ „ „ $-41°·5$	$=576·2522$
C.	„ „ „ $-42°$	$=576·2639$

Deducting the mercury, the quantity of which remained constant throughout, it appears that the flask contained of alcohol :—

		grms.
A.	at $-39°$	17·2676
B.	„ $-41°·5$	17·3169
C.	„ $-42°$	17·3286

From the data in (10) these weights represented at the respective temperatures the following volumes :—

	cub. centims.
A	20·2865
B	20·3061
C	20·3122

From the data in (4) and (5) we get the capacity of the flask up to the mark at the same temperatures :—

	cub. centims.
At $-39°$	59·6609
„ $-41°·5$	59·6568
„ $-42°$	59·6560

Subtracting the volume of alcohol in each case, that of mercury was,

	cub. centims.
In A	39·3744
„ B	39·3507
„ C	39·3438

Hence the specific gravity as obtained

In A	14·1954 at $-39°$
„ B	14·2034 „ $-41°·5$
„ C	14·2064 „ $-42°$

(12) By comparing these numbers in pairs, we have as the difference apparently due to a difference of temperature of 1° C.* :—

From A and B	·0032
„ B and C	·0060
„ A and C	·0037

of which the mean is ·0043.

Reducing, by using this coefficient, the above results to a single temperature, and adopting that of the fusing-point of the metal as determined by Balfour Stewart, we get

From A	14·1948 at $-38°·85$ C.
„ B	14·1920 „ „
„ C	14·1929 „ „

* Of course really including errors in determination of weights and temperatures.

and, as a final mean of these three, 14·1932 *as the number representing the density of solid mercury at its fusing-point as referred to water at 4° C. taken as unity.* I think this result (which, it will be seen, differs considerably from the figures hitherto quoted) may be fairly accepted with confidence.

In these experiments most of the weighings were made by Adjunct Professor Dunnington, and the freezing-mixtures were managed, at no small cost of personal discomfort, by Messrs. Bryan and Memminger, students in this Laboratory. To these gentlemen my thanks are due.

GEOLOGICAL SOCIETY.

[Continued from p. 77.]

June 20th, 1877.—Prof. P. Martin Duncan, M.B., F.R.S., President, in the Chair.

The following communications were read:—

1. "On a hitherto unnoticed circumstance affecting the piling-up of Volcanic Cones." By R. Mallet, Esq., F.R.S., F.G.S.

After some remarks upon the two forms of volcanic activity, the earlier system of "fissure eruption," and the present one of "eruption at explosive foci," which he did not think could be carried back much beyond the Tertiary epoch, the author discussed the ordinary method of formation of a volcanic cone, and pointed out that the effect of the piling-up of material must produce a pressure on the original surface commensurate with the amount of material heaped up on it, and therefore increasing gradually from the circumference nearly to the centre of the cone, where the loftiest column of material presses upon the unit of space. When the supporting rock is unyielding, such as the granite which bears the Puys of Auvergne, it will probably maintain its original position; but when it is of a more yielding nature, as in the case of the ordinary stratified rocks, the pressure of the cone will produce a saucer-shaped depression, deepest in the centre where the greatest pressure occurs; and this tendency to sink will be aided materially by the honeycombing and evisceration of the subjacent rock-masses exposed to the action of the volcano. The consequence of this depression of the surface supporting the cone will be to diminish the original slope of the successive superimposed deposits, and even in some cases cause the lowest beds to slope from the circumference towards the centre. If the strata upon which the volcano stands be particularly plastic, its pressure may cause an uprise of the strata into protuberances round the foot of the mountain. Similar phenomena may occur when the support of the cone is formed by older volcanic deposits.

2. "The Steppes of Southern Russia." By Thomas Belt, Esq., F.G.S.

The author describes sections of strata in the south of Russia, and traces the following succession of events:—

1. Deposition of marine Miocene beds when the Vienna basin and the Aralo-Caspian area were joined together, and had free communication with the Mediterranean.

2. Interruption of the communication with the Mediterranean, and deposition of the Sarmatic beds in a closed sea-basin.

3. Gradual freshening of the water of this area and deposition of the Congerian strata.

4. Lowering of the water of the Vienna basin and Aralo-Caspian area to below the present level of the ocean, and great denudation of the preceding strata. The author thinks that the drainage was at this time to the north.

5. Interruption of drainage to the north and deposition of fluviatile beds, with freshwater shells of existing species and remains of the Mammoth and Irish Elk.

6. Drainage to the north completely stopped and formation of a great lake, over which floated icebergs with northern drift. Formation of diluvial clay of the south and boulder clays of the north of Russia.

7. Lake gradually lowered by the cutting through of the channel of the Bosphorus.

The author considers that the formation of the great lake was due to the ice of the glacial period flowing down the beds of the Atlantic and Pacific, and damming back the drainage of the continents as far as it extended. To the rising of these waters he ascribes the destruction of palæolithic man, the mammoth, and the woolly rhinoceros, which he considers are prediluvial. This lake was once suddenly and torrentially discharged through the breaking away of the Atlantic ice-dam, causing the outspread of the middle glacial sands and gravels, but was formed again, and ultimately drained by the cutting through of the channel of the Bosphorus.

He also offers suggestions to account for the preservation of the Aralo-Caspian fauna and the arrival of Arctic animals in the area.

3. "The Glacial Period." By J. F. Campbell, Esq., F.G.S.

In this paper the author gave the results of numerous observations extending over many years, and made in many different parts of the world, the results of which had led him to form the opinion that no geological record exists of any abnormal Glacial periods colder than the present world's climate. But if the term "Glacial period" be used with a limitation, such as "local," or "Alpine," or "European," he saw nothing to object to. Changes in the relations between the surface of the earth and the undoubtedly permanently glacial portions of the atmosphere, principally brought about by changes of level in the former, appeared to him sufficient to account for the phenomena. The most recent so-called Glacial periods being fixed in Postpliocene times, the author remarked that Indian glaciers (lat. 27°–32° N.) are now almost as large as they have been since the deposition of the crumpled Tertiary deposits known as "Nahuns" and "Sivaliks." A similar result was obtained from observations in the Caucasus (lat. 40° N.) and Rocky

Mountains (lat. 36°–37° N.). In Northern Italy (about lat. 45°–46° N.) glaciers were a great deal larger in Postpliocene times than at present.

4. "The Action of Coast-ice on an oscillating area." By Prof. John Milne, F.G.S., of the Imperial College of Engineering, Tokio, Japan.

In this paper the author described the results of observations made by him in Newfoundland, Labrador, and Finland, which had led him to believe that many of the marks generally regarded as furnishing evidence of the existence of an ice-cap, or at least of an enormous extension of land-ice at certain periods, might easily be explained by the action of coast-ice upon an oscillating, and especially a rising area.

XX. *Intelligence and Miscellaneous Articles.*

ON THE SPECTRUM OF THE ELECTRIC SPARK IN A COMPRESSED GAS. BY A. CAZIN.

IT is generally admitted, from the observations of Wüllner, Frankland, Lockyer, and Cailletet, that the spectral lines of an incandescent gas become more and more spread as the pressure is augmented, and under a sufficient pressure unite to form a continuous spectrum. I am led by my own observations upon air and nitrogen to the following proposition:—"The electric spark in a gas is analogous to the flame of an ordinary hydrocarbon." In each of these sources of light there are gaseous particles, which produce a line spectrum, and solid or liquid particles, which produce a continuous spectrum. In the spark the latter come from the electrodes, and from the sides when these are very close. When the pressure is increased, these particles become more abundant, their continuous spectrum grows brighter, and at last causes the line spectrum of the gaseous particles to disappear.

It is in the fiery trail that things happen thus; the paler luminous sheath called the aureole is formed of gaseous particles, the line spectrum of which is more or less visible: it is to the total spark what the blue base of the flame of a taper is to the entire flame.

My first experiments on this subject are of the month of May 1876, and were at that time communicated to the Société Philomatique. I observed the spectrum by means of an ordinary spectroscope with a single, very dispersive prism. The gas was compressed in a glass tube by aid of a sort of mercury piezometer. A platinum wire is soldered to the upper end of the tube; a second wire, similar, is kept, inside, parallel to the preceding by an iron wire fixed to the bottom of the tube and which dips in the mercury. A large Ruhmkorff coil produces the spark between the platinum wires; and its image is thrown by a lens upon the slit of the spectroscope.

At the ordinary pressure, in nitrogen, the spark is pale and ridged with little strokes of fire; in the spectroscope, upon the wires are seen the channellings attributed to nitrogen, and in the intervals between these the principal lines of that gas. On compressing, one sees the channellings gradually fade, while the lines grow fainter and the continuous ground of the spectrum becomes brighter. At two atmospheres there are only six nitrogen-lines from the orange to the blue, and five diffuse bands beyond. At ten atmospheres there remain only two nitrogen-lines, $\lambda=567$ and $\lambda'=500$, and then a brilliant line in the violet ($\lambda''=424$), which made its appearance at five atmospheres, and which from my last experiments I attribute to nitrogen. The sodium-line is very distinct, while it was not to be distinguished at the ordinary pressure, which makes evident the part played by the wall of the tube. About 15 atmospheres the spark becomes dazzling; upon the continuous spectrum the four preceding lines are caught sight of, and some bright points which are due to platinum. The pressure was carried up to 40 atmospheres without these peculiarities ceasing to be distinguished.

When the gas was reduced to the ordinary pressure, the spectrum resumed its primitive aspect, but the sodium-line persisted upon the negative electrode; when the current was reversed, this line instantaneously passed from one electrode to the other, as if a sodium-compound had been electrolyzed. Further, in air compressed above 30 atmospheres the spark produced intense shining vapours, and the spectroscope showed the absorption spectrum of hyponitrous acid. It was a very fine spectrum, although the absorbing layer was less than 3 millims. in thickness.

The observation of the above phenomena is very fatiguing; and it is impossible to seize all the details, to reproduce them in an accurate drawing. The irradiation-effects dim the sight; and judgments upon the real condition of the spectrum cannot be correct. Photography permitted these inconveniences to be avoided. To it I had recourse, and succeeded in obtaining plates sufficiently delicate to favour precise measurements; and at the same time I found my opinion, on the state of the electric spark in a gas, confirmed in a striking manner.

I made use of an ordinary spectroscope with only one flint-glass prism, replacing the eyepiece by a small dark chamber. I operated upon either wet or dry collodion, according to the duration of the pose, which varied from fifteen minutes to one hour. The spectrum is photographed from the line F to the line M; and its intensity between the lines G and L is remarkable. I recognized the principal lines by photographing side by side on the same plate the solar spectrum and that of the spark, taking advantage of Ångström's Plates completed by Mascart and Cornu for the former.

The following, for example, are the results relative to the part of the nitrogen-spectrum comprised between G and H. The gas is at the ordinary pressure, in a metal cylinder with a glass plate;

and the spark, condensed by nine jars, springs between two small knobs of platinum. The sides have no effect, because of their distance. Only the principal lines are quoted; the plate contains 76. The intensity varies from 1 to 6.

*	λ=434·8	5, spread.		λ=411·8	5.
	432·5	3.		411·0	3.
	431·4	4.		410·2	4.
	429·9	2.	*	409·5	4.
	428·7	2.		407·6	4.
	427·4	4, spread.		406·9	4, double.
*	423·8	6, spread.	*x*	406·5	3.
	422·0	4.	*x*	406·2	3.
	420·7	3.		405·7	2.
	419·1	3.	*x*	404·9	5.
*	417·5	4, spread.	*	404·2	5.
x	416·2	4 (2 in the		403·5	4.
	415·2	4. [middle).	*x*	402·6	3.
	414·3	4.	*	399·6	6.
	413·1	4.		398·0	2.

The lines indicated by an asterisk have been already noted as belonging to nitrogen; the others have not before been observed. Among these, those which are indicated by the letter *x* are not produced in air with knobs of tin; the rest are common to both spectra, and consequently belong to nitrogen or hydrogen. Most of the *x* lines are more intense at the extremities than in the middle; the spectrum obtained with knobs of tin showed that the lines of the electrodes present this peculiarity. This effect is rendered most apparent by placing the spark parallel to the slit of the spectroscope.

In the chief experiment which remains to be described the spark is perpendicular to the slit. We have then on the photograph some short lines, and long ones which extend on both sides beyond the median band of the spectrum. After operating on nitrogen at the ordinary pressure, I compressed the gas in the cylinder to eight atmospheres, and took a photograph without making any change in the apparatus. The comparison of the two proofs obtained at 1 and at 8 atmospheres fully confirms my proposition. At 1 atmosphere the nitrogen-lines extend on both sides of the median region impressed by a feeble continuous light; throughout their length they are admirably sharp, since more than thirty of them could be measured in the space of 3 millimetres.

At 8 atmospheres the median region is quite continuous, and the lines of the gas can hardly be distinguished there; but these extend in both directions as in the preceding spectrum, and preserve their sharpness. This is precisely the effect which would be produced by a trail of fire formed by solid particles of dust and encompassed by an aureole of luminous gas.

I am pursuing these researches, as far as the means at my dis-

posal permit; and I hope to be able soon to make known the entire spectra of the principal simple gases.—*Comptes Rendus de l'Académie des Sciences*, May 21, 1877, tome lxxxiv. pp. 1151–1154.

PHOTOMETRIC RESEARCHES ON COLOURED FLAMES.

BY M. GOUY.

To continue these researches, I had, in the absence of any data on the subject, to make a preliminary study of the conditions on which the brightness of coloured flames depends: the most important are the thickness of the flame, its composition, the nature of the salt, and the quantity of it carried along in the combustible mixture. The apparatus employed has been described in the *Comptes Rendus**.

1. The augmentation of brightness of a line when the thickness of the flame becomes twice as great is easily deduced from the experiments described in a previous Note. That result, controlled and completed by another method, leads to this relation:—When the thickness of the flame is augmented by a fraction $\frac{1}{n}$, the brightness of the line increases by the fraction $\frac{k}{n}$; k is equal to 0·35 for sodium, 0·45 for lithium, and is comprised between 0·9 and unity for the bands of calcium and strontium. This coefficient diminishes a little in proportion as the brightness of the flame increases. The formula is inapplicable for $n<1$; it supposes also that the flame is homogeneous—which can be secured by viewing it a little above the orifice.

2. If the flame is a little overcharged with illuminating gas, and this be gradually diminished, the brightness is seen to increase, pass through a maximum, and rapidly diminish. With lithium the augmentation of brightness is scarcely noticeable, the maximum takes place before the flame ceases to be reducing (for a copper wire), and is followed by a rapid diminution. With a large excess of air the spectrum disappears. Calcium, barium, and strontium behave in the same manner; this fact appears unfavourable to the opinion which attributes the bands of their spectra to oxides. With sodium, on the contrary, the brightness of the flame augments rapidly as it becomes less reducing, the maximum is produced at the instant when it ceases to be so, and is followed by a reduction of brightness much slower than with the other metals—so that a flame containing soda and lithia is red with an excess of illuminating gas, and yellow with an excess of air.

These results are confirmed by other experiments made with one and the same flame, which can at will be made to burn in air

* See t. lxxxiii. p. 269, and t. lxxxiv. p. 231 (Phil. Mag. [5] vol. ii. p. 317, & vol. iii. p. 238).

or in a current of illuminating-gas. The oxidizing layer which enveloped the flame is thus rendered reducing; and we observe that a flame a little reducing augments the light of lithium and diminishes that of sodium.

3. It was first ascertained that solutions diluted to $\frac{1}{100}$ are converted to powder and carried along by the gaseous mixture in the same quantity, whatever be the substance dissolved. For that purpose a crystal of nitrate of calcium is added to a portion of a solution of nitrate of strontium; the liquid gives the spectrum of strontium with the same brightness as the original solution. The experiment repeated with other salts gives the same results. It is therefore sufficient, in order to compare salts having the same base and different acids, to prepare dilute solutions of them containing the same quantity of metal per litre and submit them to experiment. Each salt is compared with the nitrate by pulverizing each of the two solutions alternately, and thus making four or six cross experiments. Here is a series of measurements made with a slightly reducing flame, at 1 centim. above the orifice:—

	Nitrate.	Acid sulphate.	Chloride.	Bromide.	Iodide.	Phosphate.	Carbonate.	Tartrate.
Sodium ..	1	1·001	1·010	0·991	0·990	1·013	0·998	1·014
Lithium ..	1	1·003	0·992	1·008	1·009	0·996	...	0·992

The differences are of the order of possible errors; therefore the brightness of the spectrum, of these two metals, does not depend on the element with which the metal was combined. Nor has a slight excess of acid any more influence; but with a notable quantity of chlorhydric acid, bromine, &c. the brightness is diminished.

Calcium and strontium present some remarkable peculiarities. Their acid phosphates give but a very feeble spectrum. Nitrate of calcium gives a more feeble spectrum than the other salts—chloride, bromide, iodide, acetate*; the ratio varies from 1·47 to 1·93, and is the same for the principal bands. Moreover, for one and the same salt, the ratio varies with the conditions of the experiment. It must be remarked that the lines proper to the chloride and the other non-decomposed salts are not visible; all the salts give the same spectrum.

The deportment of the salts of strontium is the same, but with less variations. The brightness of the spectrum being equal to 1 for the nitrate, it varies from 1·2 to 1·5 for the other salts.

4. From what we have just seen, the quantities of salts introduced into the flame are in the same ratio as the richness of the solutions employed. Thus, when the quantity of salt introduced

* It was ascertained that these differences do not depend on unequal pulverization, by dissolving in each of the liquids the same quantity of a salt of sodium or lithium; the lines of these metals had the same brightness.

is doubled, the increase of brightness of each line is, at the most, equal to that which would be produced by doubling the thickness of the flame, and is almost always inferior to it. We have to remark that the quantity of free metal in the flame is not necessarily proportional to the quantity of salt which it contains; it seems to follow from the comparison just made that it increases less quickly. I purpose to return to this point when I have finished the study of certain anomalies presented by these experiments.—*Comptes Rendus de l'Académie des Sciences*, July 9, 1877, tome lxxxv. pp. 70–72.

ON A NEW METAL, DAVYUM. BY SERGE KERN.

At the end of last month I succeeded in isolating a new metal belonging to the platinum group; I have named it *davyum*, in honour of Sir Humphry Davy the eminent English chemist.

The platiniferous sand treated had the following composition:—

Platinum	80·03
Iridium	9·15
Rhodium	0·61
Osmium	1·35
Palladium	1·20
Iron	6·45
Ruthenium	0·28
Copper	1·02
	100·09

For the separation of the metals, the ores (600 grammes) were treated by the analytical method of Professor Bunsen. The mother-liquors obtained after the separation of rhodium and iridium were heated with an excess of chloride and nitrate of ammonium. A deep-red precipitate was obtained; after calcination at a red heat it gave a greyish mass resembling platinum sponge. This, fused at the oxyhydrogen blowpipe, furnished a metallic ingot of a silver colour, and weighing 0·27 gramme. The density of davyum is 9·385 at 25° C.; the metal is hard, but malleable at a red-heat.

Davyum is readily attacked by aqua regia, and very slightly by boiling sulphuric acid. Caustic potash (KHO) produces a yellow precipitate. Sulphuretted hydrogen, passed through a dilute solution of chloride of davyum, produces a brown precipitate, which, after desiccation, takes a black colour. Sulphocyanide of potassium (KCyS), with a dilute solution of chloride of davyum, becomes red. This reaction is identical with that given by the salts of peroxide of iron. If the solutions of davyum and KCyS are concentrated, a red precipitate is obtained.

I think that, in the classification of the elements proposed by M. Mendeleeff, davyum is the hypothetical element placed between the metals molybdenum (Mo) and ruthenium (Ru). In that case the equivalent of davyum should be 100.

I hope to be able, in a few months, to communicate the results of my fresh investigations on the physical and chemical properties of davyum. The new metal appears to be a rare element in nature; platiniferous sand does not contain more than 0·045 of davyum.—*Comptes Rendus de l'Académie des Sciences*, July 9, 1877, tome lxxxv. p. 72.

ON THE DIAMAGNETISM OF CONDENSED HYDROGEN.

BY R. BLONDLOT.

Palladium charged with hydrogen acquires, as is known, the properties of a true alloy. After Graham had discovered this singular body, to which he gave the name of hydrogenium-palladium, he endeavoured to determine its physical constants. His examination extended to its magnetic properties; but there observation seemed to falsify completely the previsions of the illustrious chemist. In fact, it is known that palladium is feebly magnetic, while gaseous hydrogen was classed by E. Becquerel and Faraday among diamagnetic bodies; therefore, in palladium charged with hydrogen, one might have expected to meet with magnetic properties less marked than in palladium not charged. What happened was the opposite of this. Graham ascertained that a piece of palladium is attracted by the pole of a magnet much more powerfully after being impregnated with hydrogen by electrolysis *; and thence be concluded that hydrogenium-palladium is more magnetic than palladium.

G. Wiedemann, in reporting in his treatise on galvanism and electromagnetism † the preceding experiments, refuses to admit the conclusions drawn from them, attributing the phenomenon observed to the impurity of Graham's palladium, which "must have contained oxide of iron; the reduction of that oxide by the hydrogen exalted its magnetic properties—which accounts for the anomalies observed."

In view of this disagreement it seemed to us expedient to submit the question afresh to the test of experiment. The method we employed is that which was devised by M. Becquerel for the determination of specific magnetisms. The body for experiment, in the form of a small bar or strip, is suspended between the poles of the electromagnet by a torsion-thread so as to make a determinate angle with the line of the poles; the current is caused to pass; the bar is deflected; and to bring it back to its first position it is necessary to twist the thread at its upper part a certain angle, which, after suitable reductions, gives the measure of the specific magnetism sought.

* See *Comptes Rendus*, Jan. 18, 1869, p. 101; Phil. Mag. Feb. 1869, [4] vol. xxxvii. pp. 128, 129.

† *Die Lehre von Galvanismus und Electromagnetismus*, vol. ii. p. 553.

We operated first upon commercial palladium. A rectangular strip of palladium not charged, suspended as above described, required a torsion of 16° to bring it back to its initial position. It was then charged and replaced; this time the deflection was perfectly inappreciable with our apparatus. The strip having been discharged, heated to redness, resumed its magnetism. The experiment, when repeated with specimens of the most diverse origin, constantly gave the same result; a strip prepared by electrolysis from chloride of palladium behaved precisely in the same manner.

It necessarily follows from these experiments that charged palladium is less magnetic than uncharged, which leads us to attribute to condensed hydrogen energetic diamagnetic properties. It must therefore be admitted that, as M. Wiedemann supposes, an accidental cause may have deranged Graham's experiments. For our part, we should be inclined to accuse the impurity of the acid used to acidulate the water employed to charge the palladium by electrolysis: the least trace of a ferruginous compound gives rise to a deposit upon the palladium, which would account for the result found by Graham.

Once in possession of the fact revealed by the measurements above reported, we sought to make it evident by means of experiments more simple and more easily repeated.

Two similar strips are cut from the same piece of palladium; and then one of them is charged with hydrogen. This done, the strips are arranged crosswise, and suspended by a cocoon-thread between the poles of a Ruhmkorff electromagnet; the uncharged strip always takes the axial position. Still more simply, an elongated rectangular strip is charged only in one half of its length; suspended by a cocoon-thread in front of one pole only, the part not charged always turns towards the magnet.

These two experiments point, like our measurements, to this fact, that condensed hydrogen possesses relatively powerful diamagnetic properties. In concluding, we will remark that it is not unimportant in regard to theory to know that the condensation of a diamagnetic body has rendered it more diamagnetic under the same volume. Tyndall, in his researches on crystallized bodies, was led to admit analogous facts, and to draw from them important arguments for the existence of diamagnetic polarity*; his presumptions are found, as we see, perfectly justified by experiments.—*Comptes Rendus de l'Académie des Sciences*, July 9, 1877, tome lxxxv. pp. 68, 69.

* Phil. Mag. [4] vol. ix. p. 208 (March 1855).

THE

LONDON, EDINBURGH, AND DUBLIN

PHILOSOPHICAL MAGAZINE

AND

JOURNAL OF SCIENCE.

[FIFTH SERIES.]

SEPTEMBER 1877.

XXI. *On the Magnetic Behaviour of Chemical Compounds.* By Professor G. WIEDEMANN*.

SCARCELY twenty-five years have elapsed since, in chemistry, the so-called theory of types united in its artificial scheme the special theories of radicals and of substitution (in which the earlier experiments found a first hypothetical expression), and thereby rendered possible the discovery of a great number of new compounds, the composition of which fitted perfectly into the once-given formulary. These scientifically valuable results misled not a few chemists to regard, with a certain fanaticism, the new doctrine as an almost irrefragable gospel of chemistry, even though on the part of others the arbitrary equalization of elements which in the compounds stand in the most decided electrolytic opposition, the parallelism of utterly heterogeneous compounds, &c. was at the same time looked upon as in the highest degree problematical.

Again after barely ten years, in a perfectly natural process of evolution, especially in consequence of greater attention to the regularities expressed in the notion of *valency* introduced into the law of multiple proportions, that theory was replaced by the structure theory. Its solid classification, apparently resting on such simple principles, its far more important consequences in the production of an extraordinarily great quantity of substances ranging themselves under it and especially more valuable for the arts, gained for it the adhesion of the

* Translated from the Decanal Dissertation prefixed to the List of Doctors of Philosophy and Masters of Arts created by the Leipzig University in the Academical year 1875–1876, communicated by the Author.

former professors of the type theory; and in many quarters it is regarded as the firm and final foundation upon which the edifice of our chemical science has to be built. If in particulars views sometimes differ, yet upon the whole the structure theory is believed to express decisively the constitution of chemical compounds, the placing of their atoms. Nay, some have even gone so far as to wish to render the latter in symbolical representations; and in consequence of this, a few individuals have esteemed the schematic notation of the bonds on a plane surface not sufficient, the molecule being corporeal—an error which can only have resulted from a strange confusion of symbol with reality, the figurative representation of the supposed reciprocal binding of the atoms with the shape of the molecule consisting of them.

It is frequently held that a purely chemical investigation is sufficient, without the measurement of vapour-density, to establish the relative positions of the atoms in compounds in the sense of the structure theory. Corresponding to this method of investigation, besides the molecular weight, the structural formulæ represent, although in a very complete manner, yet only the processes out of which they have resulted; they mark the groups of atoms which, on the various chemical attacks (heating &c.), separate from the combinations or are exchanged with others. Meanwhile other questions are:—whether, beyond these limits of direct observation, the fundamental hypotheses of the structure theory (often not a little complicated notwithstanding their apparent simplicity) can be brought into harmony with the principles of general mechanics; and how far it can account for the physical properties of the compounds, which properties must yet result immediately from their chemical constitution.

This is not the place to enter upon a more special reply to these questions, of which especially the first would require a very detailed discussion. In regard to the second we will only cursorily mention that in fact the structural formulæ indicate very well in isolated cases certain regularities in the physical properties. Thus the isomorphism of some substances coincides with the analogy of their formulæ (KNO_3 and $CaCO_3$, &c.). The repeated entry in like manner of CH_2 into the formulæ of the fatty acids, alcohols, aromatic compounds, with the normal twofold binding of the carbon atom of that group to two other carbon atoms, corresponds to a like alteration of the boiling-point, the molecular volume, the refraction-equivalent: the latter constants are different with isomeric compounds of different structure, &c.

On the contrary, the structural formulæ do not in any way

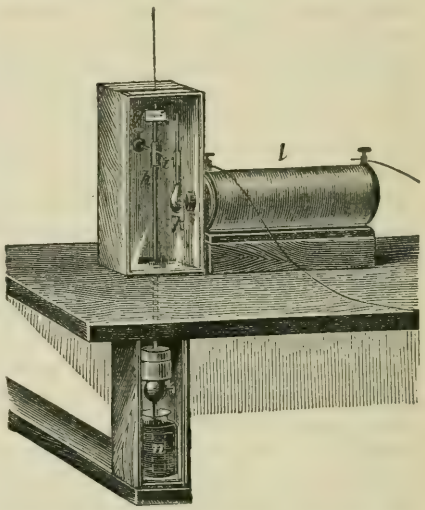
conform to the electrolytic deportment of the compounds. While in the case of non-electrolyzable substances considerations upon electrical contrarieties of their constituents, without experimental foundation, can only be the subject of purely theoretical speculations, the separation, effected by the same current, of various electrolytes into their ions proves that the latter contain equal quantities of positive or negative electricity (are electrolytically equivalent). This equivalence is not everywhere expressed by the structural formulæ: thus in the compounds $FeCl_2$ and Fe_2Cl_6 equal quantities of chlorine (2 Cl), on the one hand, and the different quantities of iron (Fe and $\frac{2}{3}$ Fe) combined with them, on the other, are equivalent. It is the same with chloride of potassium and the yellow prussiate of potash, to which are assigned the formulæ KCl and $4K + FeCy_6$, while yet the equivalence of equal quantities of potassium in them is ascertained, and so on. These electrolytic relations of the compounds, however, would surely have as much right to be taken into account, in the consideration of their structure, as their chemical properties; and it is obvious that a complete knowledge of the constitution must give a full account of them as well as of the latter.

Similar relations present themselves on the consideration of the magnetic properties of compounds. While in the chemical and electrolytic investigation of bodies it is always the result of a displacement or separation of their atoms that is discovered, and consequently only at the beginning and end of certain states of motion is the way in which they are combined considered, the magnetic investigation of compounds offers the advantage that we can study a physical property altogether characteristic of the individual atoms of the compounds without any decomposition, on the unaltered compounds, and can therefore draw a conclusion respecting the particular behaviour of those atoms in them.

Permit me, in the following, to epitomize the communications which I have previously published on the magnetic behaviour of chemical compounds, together with an account of more recent observations on the same subject. Perchance this combination may furnish a fresh instance of even a purely physical method of investigation sometimes giving a revelation, in certain directions, respecting the constitution of chemical compounds, such as could never be attained through purely chemical reactions exclusively.

The magnetic moment of the bodies experimented on was measured by means of a torsion balance. The head of it could be rotated about its axis, in a vertical hollow cylinder, by

means of a horizontal endless screw gearing into its edge and turned by a cord led to the observer. To the head was suspended, by a very hard-drawn German-silver wire of 0·2–0·3 millim. thickness, and 640 millims. length, a vertical brass rod, *h*, 550 millims. long and 5·5 millims. thick, loaded beneath with weights (about a kilogram), and furnished at its lower extremity with vanes which were immersed in a glass vessel *n*, filled with oil, in order to damp the oscillations of the apparatus. On the brass rod, about 70 millims. below its upper end, a horizontal arm, *i*, 20 millims. long, was fastened, filed outquadrangularly in front, so that exactly fitting quadrangular brass rods could be inserted in it, which supported in a brass holder little flask-shaped glass vessels, *k*, balanced by a counterpoise. The glass vessels were partly spherical, partly flattened, so that their plane surfaces were parallel with the vertical plane pasing through the brass rod and the arm. These vessels were filled, up to a mark on the neck, with the substances to be investigated. In the position of rest the arm *i* was in the magnetic north-and-south plane. In front of the glass vessel *k* a very powerful electromagnet, *l*, was placed in an east-and-west position: in the more recent experiments it consisted of an iron core terminating in front in a truncated cone, of 320 millims. length and 70 millims. diameter, placed in a helix of 1200 turns of covered copper wire 2·5 millims. in thickness. Its magnetic moment, J, was determined, by means of scale and telescope, from the deflections of a steel magnetic needle suspended in a thick copper box, set up in the direction of the prolongation of the axis of the magnet, at a distance of 230 centims. from its fore end.



A mirror, *g*, fixed to the brass rod *h*, permits the orientation of the apparatus to be observed by means of a scale at the distance of 2 metres and a telescope. First its *nil*-position was determined without the magnet's influence; then the magnet was excited, its moment, J, determined, and by turning the

head of the torsion balance the apparatus brought back to *nil*. After the opening of the magnetizing current the apparatus rotated back, in consequence of the torsion of the German-silver wire, through an angle T. The value $M = \frac{T}{J^2}$ then measures, in each case, the magnetic moment of the glass flask, and the contained substance, for the unit moment of the magnet acting upon them. In this way, first, the following preliminary determinations were carried out:—

1. *Influence of the Magnetizing Force.*—If a solution of sulphate of iron was exposed to the action of various magnetic forces (78·8, 116, 150·3, 181·8, 208·5), the value M changed only in the ratio from 8583 to 8621, and irregularly, with a rising intensity of the current. Therefore, *within the limits of the observations, the magnetic moment of the vessel filled with sulphate-of-iron solution is directly proportional to the magnetizing force acting upon it.*

2. *Effect of Concentration.*—If the glass vessel was filled with solutions of the same salt in different degrees of concentration, and from its magnetic moment calculated for the magnetizing force 1 the corresponding negative moment of the diamagnetic glass vessel filled with water was subtracted, the magnetism of the dissolved salt was obtained. This amounted, for example, with solutions of protochloride of manganese containing 0·956, 0·717, 0·478, and 0·239, to 163, 120·3, 80·87, and 40·20 respectively.

The magnetism of salt-solutions is therefore directly equivalent to the sum of the magnetisms of the dissolving medium and the salt dissolved; and the magnetism of the latter is proportional to the weight contained in the unit of volume.

Similar results had previously been found by Plücker; deviations therefrom will be cited *infrà*.

3. *Influence of the Solvent.*—Aqueous, alcoholic, and etheric solutions of perchloride of iron showed, after deducting the magnetism of the vessel and solvent, nearly the same magnetism for the unit of the dissolved salt.

The magnetism of the dissolved salt by itself is therefore nearly independent of the nature of the solvent.

4. *At different temperatures*, t, with a series of salt-solutions (for example, of ferrous sulphate of different degrees of concentration, protochloride of iron, perchloride of iron, nickelous sulphate, cobaltous nitrate, and red prussiate of potash) the magnetism of the salt, m_s, by itself, after deducting the magnetism of the solvent, was expressed by the formula

$$m = 100 - 0{\cdot}325\,t,$$

the magnetism at 0° being put equal to 100.

Therefore, so far as can be concluded from the preceding observations, *the magnetism of the dissolved salt diminishes proportionately with the rise of temperature, and, for all the salts hitherto investigated, notwithstanding their great chemical difference, according to the same law.*

The number 0·325 coincides approximately with the coefficient of the diminution of electric conductivity of the metals with rise of temperature.

5. *Magnetism of various Salts dissolved in Water.*—If the magnetism calculated for the unit of weight of the salts dissolved in water is equal to m, and the molecular weight of the salts A, the value $\mu = Am$ is the magnetism of one molecule of the salt in question, its *molecular magnetism.* In like manner the magnetism of each atom of the magnetic metal in the salts, its *atomic magnetism* α, can be calculated.

It has been found, as the result of numerous trials, that, with the oxygen, as well as with the haloid salts, *the molecular magnetism of the dissolved salts of the same metal with different acids is approximately the same.* Thus, for example, in an arbitrary unit, for nickelous sulphate, nitrate, and chloride, μ is = 1426, 1433, 1400; for ferrous sulphate, nitrate, and chloride, 3900, 3861, 3858; for the relatively feebly magnetic cupric nitrate, acetate, and chloride, 480, 489, 477; &c.

If the atomic magnetism of the iron in the ferric salts be denoted by 100, that of the metals of the other salts will be:—

	α		α
Manganous.....	100·4	Cupric.....	10·8
Ferrous	83·1	Cerious	10·3
Cobaltous	67·2	Ferric.....	100·0
Nickelous	30·5	Chromic	41·9
Didymic.....	22·6		

According to this, *the mean molecular magnetism of the ferrous salts stands approximately midway between the magnetisms of the manganous and cobaltous salts, and the molecular magnetism of the cobaltous salts midway between those of the manganous and nickelous.*

The molecular magnetisms of the four groups of salts mentioned (the nickelous, cobaltous, ferrous, and manganous) are, therefore, to one another in the ratio $a : a+b : a+1\frac{1}{2}b : a+2b$. One would suppose that this relation of the magnetic properties of the four groups of salts would also find expression in the series of the atomic weights of their metals; but at least the values hitherto fixed for them do not accord therewith.

6. *Magnetism of the Solid Salts.*—The magnetism of the solid salts combined with the water of crystallization is ap-

proximately the same as that of the salts in solution. Thus, if the molecular magnetism of the ferric salts in their strongly acid solutions is equal to 100, it is (when the salts contain water of crystallization):—

For manganous sulphate	100·4
„ ferrous sulphate	78·5
„ ferrous ammonium sulphate ...	83·0
„ cobaltous sulphate	67·2
„ nickelous sulphate	29·9
„ didymic sulphate	23·0
„ cupric sulphate	10·6

If the salts be deprived of water, their molecular magnetism changes in some cases more considerably. Thus, for the following anhydrous salts it is, compared with the atomic magnetism of the metal in the ferric or manganous salts taken as equal to 100 :—

Anhydrous cobaltous sulphate	67·2
„ nickelous sulphate	29·2
„ cerious sulphate	9·9
„ cupric sulphate.....	9·3
„ ferrous chloride	83·1
„ cobaltous chloride	82·9
„ nickelous chloride	33·5
„ cupric chloride	8·7
„ cupric bromide.....	5·2

The insoluble salts behave similarly. Thus the molecular magnetism for

Cobaltous phosphate is	64·0
„ carbonate	60·3
Manganous phosphate	103·9
„ carbonate	90·2

Here, however, it is to be observed that perhaps, on being washed with water, the carbonates have partially decomposed.

The equality of the magnetisms of the molecules of the different dissolved salts of the same metal, as well as the differences in the behaviour of the dissolved and the solid salts, may find their explanation in the now pretty generally accepted theory of magnetization, which has gained a sure support especially from the mutual relations between the mechanical and the magnetic behaviour of the substances.

If the magnetism of bodies is conditioned by the existence of preformed molecular magnets, which in the unmagnetic state have their poles directed to all sides, but under the

action of magnetizing forces arrange themselves all more or less in determinate directions, then the intensity of rotation of the molecular magnets in different substances under the action of the same external magnetizing forces depends, first, on the quantity of their own invariable magnetic moment, and, next, on the resistance opposed by the molecular forces to their rotation.

But we have observed, first, that in the solutions of the above-mentioned different kinds of salts of the same magnetic metal the molecular magnetism is the same. Therefore it cannot be essentially affected by the variable constituents of the salts. Indeed most of these possess, in relation to the magnetism of the majority of the salts themselves, only a very feeble magnetism or diamagnetism. The same is true also of the oxygen contained in the oxygen salts, since the haloid and oxygen salts behave precisely alike with respect to magnetism. Also the supposition, expressed by Schönbein among others, that oxygen may be contained in the salt-formers, cannot be maintained, since, for example, the copper compound of the (by itself) feebly diamagnetic ferrocyanic hydrogen acid (which certainly contains no oxygen) possesses the same quantity of molecular magnetism as the rest of the copper-salts. Accordingly the temporary magnetism of salts under the influence of magnetizing forces can only proceed from the magnetic position of the metallic atoms contained in their molecules.

We know, further, again through magnetical investigations, how very much the molecular forces operative in every individual magnetic group of molecules are affected by external circumstances, pressure for instance. If an amorphous pulveriform body were suspended at its centre of gravity in a homogeneous magnetic field, between two magnetic poles, so that the magnetic forces acted with equal intensity upon all the molecules, the body would, as under the influence of gravity, remain in equilibrium in all positions, even when the particles were brought nearer to one another by a pressure in one or another direction—provided that their magnetic action upon one another could be neglected, which would effect a diminution of the diamagnetic moment in diamagnetic, an increase of the magnetic moment in magnetic bodies. We find, however, that by one-sided pressure not only the magnetism but also the *diamagnetism* of pulveriform substances is increased in the direction of the pressure. This, therefore, cannot arise only, as was at first assumed, directly from an alteration of the density of aggregation of the molecular groups, but the groups themselves must be altered.

The salts may also exhibit a similar alteration when their density is increased by drying and heating to redness. In some cases, especially with the salts of the strongly magnetic metals, certainly at first a greater reciprocal action of the magnetically directed elements of the individual magnetic molecular groups, and therefore an augmentation of the temporary moment under an equal external force, may also be thereby conditioned—for instance, with the cobaltous and nickelous chlorides. In other cases the rotability of the magnetic elements in the individual groups of molecules may be diminished.

The effect of the alteration of the molecules in consequence of condensation might also be, that the molecular currents induced by the magnet, which condition the diamagnetic behaviour of the bodies, would, along with the turning of the magnetic atoms endowed with permanent magnetic molecular currents, come forth with greater intensity, whence, therefore, likewise a diminution of the temporary magnetism would result. This is particularly evident with the very dense cupric bromide. That through alteration of the density alone the proper magnetism of the magnetic atoms themselves is changed, is perhaps a scarcely admissible assumption.

Except in such extreme cases, however, the divergencies between the magnetisms of the dissolved and the solid salts are but slight. Accordingly we say, generally, that *with like chemical properties of the metallic atom in the molecule of different compounds its atomic magnetism is also the same.*

7. *Magnetic Deportment with Double Decomposition.*—The above result is further confirmed by the fact that *on mixing solutions which, through double elective affinity, mutually exchange their constituents, the total magnetism of the solutions is the same after as before the double decomposition.*

In the experiments made in reference to this, the flask-shaped glass vessel of the torsion apparatus was first filled up to the mark with each of the solutions to be mixed, A and B, and their magnetisms M_a and M_b, deducting the magnetism of the glass, determined, as well as their weights G_a and G_b. After this the glass vessel was partially filled with A and partly with B, so that the total volume of both together was the same as the previous volume of each. The solutions were then mixed by agitation. If the weights of the mixed solutions are g_a and g_b, if there were no reciprocal action their common magnetism, after deducting that of the glass, would be

$$M = m_a + m_b = M_a \frac{g_a}{G_a} + M_b \frac{g_b}{G_b}.$$

Experiment showed that, even when precipitates were formed, it was almost invariably likewise equal to M. Thus, among others, were observed mixtures of:—

	m_a.	m_b.	m_a+m_b.	M obs.
Ferric chloride and sulphocyanide of potassium	19·4	−4·3	=15·1	14·6
Ferric chloride and ferrocyanide of potassium	24·6	−4·1	=20·5	21·1
Ferrous sulphate and ferricyanide of potassium	38·9	+2·2	=41·1	40·3
Cuprous sulphate and ferrocyanide of potassium	4·8	−4·1	= 0·7	0·8
Cobaltous nitrate and ferricyanide of potassium	23·9	+5·3	=29·2	29·2
Cobaltous nitrate and ferrocyanide of potassium	38·5	−2·2	=36·3	35·9
Cobaltous nitrate and manganicyanide of potassium	39·7	+0·8	=40·5	41·0

Apart from the mostly very slight secondary influence of the change of density, according to this the magnetism of the binary compounds is directly composed of the magnetism of their constituents. If the latter, without altering their constitution or the grouping of their atoms, change into other binary compounds, they still preserve the magnetism proper to them.

8. *In general the molecular magnetism changes if the constitution of the compounds changes.*—The most interesting example of this kind is presented by the cupric salts, which are strongly magnetic (as, for instance, cupric chloride and cupric bromide), while the cuprous salts and also metallic copper are feebly diamagnetic. Therefore *a diamagnetic metal* (copper) *combined with diamagnetic elements* (*e. g.* bromine) *may furnish magnetic compounds.* The basis of these phenomena is perhaps to be sought in the occurrence in intensity of the molecular currents which condition diamagnetism in the molecular groups of metallic copper—groups in themselves very feebly magnetic, but formed out of well conducting copper atoms,—while in the molecules of its salts those currents do not meet with the copper atoms requisite to their formation united in equal measure.

We will subsequently produce further examples of alterations of molecular magnetism with alteration of constitution.

9. *The magnetism of the hydrates of the magnetic metals* was determined according to the same method which served

for the investigation of the behaviour of two salt-solutions with double decomposition. An aliquot part of the salt-solution the magnetism of which was investigated in the flask of the torsion-apparatus was put into the flask with a quantity of potash or soda lye, or liquid ammonia, sufficient to produce precipitation; with the latter the flask was filled up to the mark, and after agitation, before deposition, the magnetism of the hydrate determined. The calculation of the magnetism of the precipitated oxide took place as above, except only that from the magnetism of the precipitated solution that of the glass and the water, or of the soda or potash lye or the ammonia (which differed but very slightly from that of the water), was deducted.

If μ_s denotes the molecular magnetism of the dissolved salts of the magnetic metals, then the molecular magnetism μ_h of the corresponding hydrates is as follows:—

Manganous hydrate	$\mu_h = 0{\cdot}85\mu_s$
Ferrous hydrate	„ 1·12
Cobaltous hydrate.....	„ 1·12
Nickelous hydrate.....	„ 1·00
Cupric hydrate	„ 0·74
Chromic hydrate	„ 0·95
Ferric hydrate	„ 0·69–1·18

The molecular magnetism of the ferric hydrate changes, after the addition of ammonia to a solution of ferric chloride, very rapidly from the smaller value to the greater—of course in consequence of the oxide passing out of the colloid into the ordinary state (*vide infrà*).

According to this the *molecular magnetisms of most of the hydrates of the peroxides* are partly but little less or greater, partly *very approximately the same as those of the corresponding salts* in their solutions. Hence, taking into consideration the altered density-ratios, we may perhaps assume that these values would, under otherwise similar circumstances, be equal to one another; and accordingly the magnetic groups of atoms would also remain unchanged the same in both series of compounds.

10. Quite different from this is the *magnetism of colloid solutions of the oxides*. A solution of *colloid ferric oxide*, obtained by dialysis of a solution of ferric chloride digested with ferric hydrate, shows, in proportion to its content of iron, a much feebler magnetism than a neutral and concentrated solution of ferric chloride or one mixed with a large quantity of acid. The molecular magnetism of the colloid solution of ferric oxide is accordingly only about 0·21 of that of the ferric salts.

If ferric hydrate be dissolved in a not too dilute solution of ferric chloride (in which latter, according to the experiments to be subsequently mentioned, the ferric chloride continues without dissociation almost unaltered), the magnetism of the solution is composed directly of that of the ferric chloride and that of the colloid solution of ferric oxide, as well as that of the water.

Such a solution contained 0·177 gram of iron in the ferric chloride, 0·020 gram of iron in the colloid solution of the oxide. Its observed magnetism was equal to 30·07, while the magnetism of an equal volume of a solution of ferric chloride, which contained 0·394 gram of iron, was 68·31, and that of a solution of colloid ferric oxide, which contained 0·204 gram of iron, was 7·56. According to this the magnetism of the ferric-chloride solution containing the oxide is calculated at $\frac{0{\cdot}020}{0{\cdot}204} \times 7{\cdot}56 + \frac{0{\cdot}177}{0{\cdot}394} \times 68{\cdot}3 = 0{\cdot}74 + 30{\cdot}68 = 31{\cdot}42$, which is not far from the value found. From the diminution of the magnetism of a dissolved ferric salt, especially the salts of the organic acids, it can in other cases be proved that a greater or smaller portion of it is decomposed into colloid ferric oxide and acid by dissolving (see further on).

If to a solution of sal ammoniac in ammonia freshly precipitated chromic hydrate be added, the latter dissolves. producing a deep-dark-red solution. Its magnetism, obtained in the round glass vessel, was as stated in the following Table, in which G denotes the weight of chromium in 10 cubic centims. of the solution, M the magnetism of the solution after deducting those of the vessel and the water or of the sal-ammoniac solution, α the atomic magnetism :—

	G.	M.	α.
Chromic oxide in sal ammoniac.....	0·482	155	35·1
Ferric nitrate	0·473	453	100

The magnetism of the chromium in this solution is therefore but little inferior to (about 0·9 of) that of the chromium in the chromic salts (4·9).

When chromic oxide is dissolved in potash solution, it retains exactly the same magnetism as in its combinations with acids. Thus the magnetism of 20·42 grms. of a solution of chromic nitrate in the round glass, after deducting the magnetism of the glass, was equal to 44·3 ; that of 19·25 grms. of potash lye was, in like manner, equal to −6·6 ; that of the chromium in a mixture of 4·72 grms. of salt-solution and 13·27 grms. of potash lye was equal to 11·1, while the calculation of the magnetism of the chromium in the solution as it corresponds to the magnetism of the salts gives the

number 11·7. The magnetism of the dissolved chromic oxide was therefore about 0·94 of that of the chromic oxide in the salts, and nearly equal to that of the precipitated chromic hydrate: accordingly we cannot well assume that here the chromic oxide is dissolved in the colloid state; it is much more probable that the chromium in the alkaline solution is approximately in the same state as in the peroxide-salts.

If the chromic salts, *e. g.* chromic nitrate, be regarded as consisting of $Cr_2+(NO_3)_6$, then in all salts in which chromium in like manner enters into a combination with an electronegative radical its atomic magnetism should be the same. But if the solution of chromic oxide in potash were also to be looked upon as the solution of a salt $K_2+(O+Cr_2O_3)$, the chromium would then be in quite another group of atoms than that in which it was before, and it is fore-evident that its magnetism must likewise be quite different; its equality in the alkaline solution of chromic oxide is perhaps a proof that the chromic hydrate is dissolved as such unaltered in the potash lye, and that it does not enter into a special electronegative group of atoms combined with the electropositive metal potassium to form a saline compound.

Precisely similar is the behaviour of the alkaline solutions of the salts whose precipitation by potash &c. is prevented by the addition of organic substances—for instance, solution of *cobaltous sulphate* mixed with grape-sugar and potash.

For example, the round glass, filled up to the mark with 19·6 grms. of solution of cobaltous sulphate, showed the magnetism 138, after deducting that of the glass and water. Then only 8·1 grms. of the solution were poured into the glass, and it was filled up to the mark with grape-sugar solution and potash lye, when no precipitation took place. After deducting the diamagnetism of the solvent (the grape-sugar containing potash lye), which differed but little from that of the water, there remained the magnetism of the cobaltous compound, equal to 57.

While, therefore, the weights of cobalt employed in the two cases were proportioned to one another as 19·6 : 8·1 (=100 : 41), the ratio of the magnetisms was as 138 : 57 (also =100 : 41). Here, then, the cobaltous hydrate is also probably dissolved unchanged; a transition into the colloid state, or the formation of special, differently grouped compounds cannot with likelihood be assumed.

[To be continued.]

XXII. *On some Effects of Dissociation on the Physical Properties of Gases.* *By* W. M. Hicks, *M.A., Fellow of St. John's College, Cambridge.*

[Continued from vol. iii. p. 418.]

[Plate III.]

IV.

22. We must now consider the case of a compound gas whose molecule is diatomic, and which is formed by the combination of two elementary gases A and B. We will denote the atoms of A and B by the letters A, B, and the molecules of the three gases by AA, BB, AB. The constants required will be eighteen—viz. the three blows required to break up AA, BB, and AB, and the mean effective distances between every pair of AA, BB, AB, A, B, the number of which is fifteen.

Let c_1, c_2, c be the respective blows required to break up AA, BB, AB, and let the mean effective distances be given by the following Table, where the arrangement is obvious:—

	AA	BB	AB	A	B
AA	s_{11}	s_{12}	s_{10}	s_{13}	s_{14}
BB	s_{12}	s_{22}	s_{20}	s_{23}	s_{24}
AB	s_{10}	s_{20}	s_{00}	s_{30}	s_{40}
A	s_{13}	s_{23}	s_{30}	s_{33}	s_{34}
B	s_{14}	s_{24}	s_{40}	s_{34}	s_{44}

Let also the numbers of AA, BB, AB, A, B be x, y, z, x', y'. Then, remembering that the masses are $2m_1$, $2m_2$, m_1+m_2, m_1, m_2,

$$\frac{dx}{dt} = \text{gain of molecules of A per unit of time}$$
$$= \text{number of collisions of A with A with blow } < c_1$$
$$\quad - \text{number of collisions of AA with blow } > c_1$$

$$= 2\sqrt{\pi\theta}\left[x'^2 s_{33}^2 \sqrt{\frac{2}{m_1}}\left\{1 - \operatorname{Exp}\left(-\frac{c_1^2}{2m_1\theta}\right)\right\}\right.$$
$$- x\left\{2x s_{11}^2 \sqrt{\frac{1}{m_1}} \operatorname{Exp}\left(-\frac{c_1^2}{4m_1\theta}\right) + y s_{12}^2 \sqrt{\frac{m_1+m_2}{2m_1 m_2}}\right.$$
$$\left.\left. \times \operatorname{Exp}\left(-\frac{m_1+m_2}{8m_1m_2}\frac{c_1^2}{\theta}\right) + \ldots\right]\right.$$

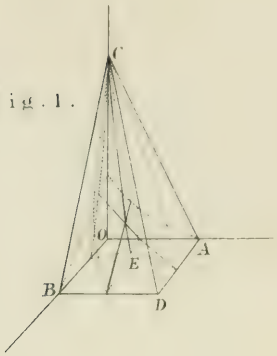


Fig. 1.

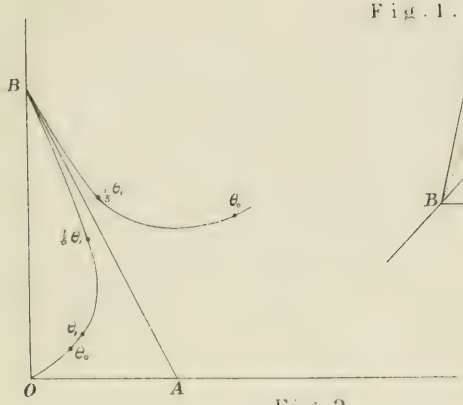


Fig. 2.

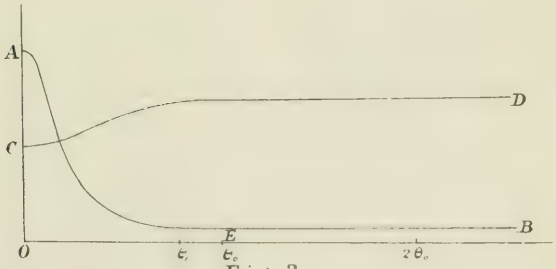


Fig. 3.

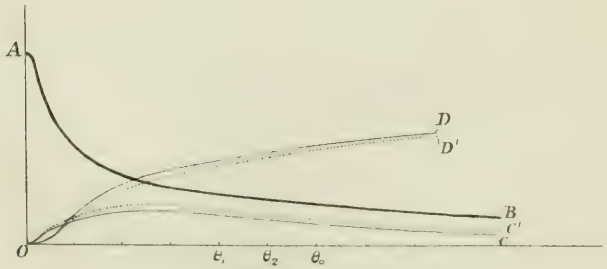


Fig. 4.

Mintern Bros. lith.

$$\frac{dy}{dt} = 2\sqrt{\pi\theta}[\dots]$$

$$\frac{dz}{dt} = 2\sqrt{\pi\theta}[\dots],$$

$2x+z+x' =$ number of A present $= N_1$ say,

$2y+z+y' \quad$ „ $\quad$ B $\quad$ „ $\quad = N_2$ say.

For the sake of simplicity we will write the above equations thus:—

$$\left.\begin{aligned}
\frac{1}{2\sqrt{\pi\theta}}\frac{dx}{dt} &= a_{33}x'^2 - x\{2a_{11}x + a_{12}y + a_{10}z + a_{13}x' + a_{14}y'\},\\
\frac{1}{2\sqrt{\pi\theta}}\frac{dy}{dt} &= a_{44}y'^2 - y\{a_{21}x + 2a_{22}y + a_{20}z + a_{23}x' + a_{24}y'\},\\
\frac{1}{2\sqrt{\pi\theta}}\frac{dz}{dt} &= a_{34}x'y' - z\{a_{01}x + a_{02}y + 2a_{00}z + a_{03}x' + a_{04}y'\},\\
2x+z+x' &= N_1,\\
2y+z+y' &= N_2,
\end{aligned}\right\} \quad (1)$$

where

$$\left.\begin{aligned}
a_{pq} &= s_{pq}^2\sqrt{\frac{m_p+m_q}{m_pm_q}}\ \mathrm{Exp}\left(-\frac{m_p+m_q}{4m_pm_q}\frac{c_p^2}{\theta}\right),\\
a_{qp} &= s_{pq}^2\sqrt{\frac{m_p+m_q}{m_pm_q}}\ \mathrm{Exp}\left(-\frac{m_p+m^q}{4m_pm_q}\cdot\frac{c_q^2}{\theta}\right),
\end{aligned}\right\} \quad . \quad . \quad (2)$$

except for a_{33}, a_{44}, a_{34}.

When the gas is in its stable state,

$$\frac{dx}{dt} = \frac{dy}{dt} = \frac{dz}{dt} = 0,$$

and we get five equations to determine the five unknowns, x, y, z, x', y'.

We can at once reduce these to three equations of the second degree in x, y, z by eliminating y', z' by means of the last two. As we shall chiefly have to do with gases mixed in their chemical proportions, we will suppose for the future that $N_1 = N_2 = N$ (say). Then dividing equations (1) by N^2, and (2) by N, we may regard x, y, z as the proportions of AA, BB, AB to the whole number of A or B present.

23. In general, from three equations of the second degree between three unknowns we shall get eight sets of solutions. But all the solutions of equations (1) may not suit our purpose. We must reject as unsuitable all imaginary roots, all negative roots, and all positive roots in which x or $y > \frac{1}{2}$, and

z, x', or $y'>1$; that is, the roots must be such that

$$x \text{ and } y>0<\tfrac{1}{2},$$
$$z,\quad 1-z-2x,\quad 1-z-2y>0<1.$$

If we regard x, y, z as coordinates of a point in space, this condition asserts that the point may lie anywhere within a pyramid whose base is a square having the axes of x and y for adjacent sides and the length of a side $=\frac{1}{2}$, and whose vertex is on the axis of z at a height 1 from the origin. It can be shown, as follows, that we always have one, and only one, solution of the above equations satisfying these conditions.

Let O A, O B, O C (Plate III. fig. 1) be the axes of coordinates, O A D B C the pyramid within which (x, y, z) must lie. The three equations (1) represent three quadrics; and we have to show that they have one, and only one, intersection within this pyramid; and this we shall do by proving that they divide the pyramid in such a way that they must cut one another at some one point within, and at only one. Taking the first, or

$$a_{33}(1-z-2x)^2-x\{2a_{11}x+a_{12}y+a_{10}z+a_{13}x'+a_{14}y'\}=0,$$

we see that it has a generating line through C parallel to O B; also it cuts both O A and B D between O, A and B, D. For, putting $z=y=0$, we have, to find x,

$$a_{33}(1-2x)^2-x\{2a_{11}x-2a_{13}x+a_{13}+a_{14}\}=0:$$

when $x=0$ this is positive, and when $x=\frac{1}{2}$ it is negative; thus there is one, and only one, root between O and A. Similarly there is one, and only one, between B and D. Thus the surface divides the pyramid into two portions by a diaphragm extending from C, and intersecting the faces C O A, C B D, and the base.

Similarly the second surface divides the pyramid by a diaphragm extending from C, and intersecting the faces C O B, C A D, and the base. Therefore they must intersect on a simple curve extending from C to a point E in the base, and lying between wholly within the pyramid.

The third quadric has B D, D A for generating lines, and also cuts O C in one, and only one, point. For putting $x=y=0$, we have, to find z,

$$a_{34}(1-z)^2-z\{2a_{00}z+(a_{03}+a_{04})(1-z)\}=0,$$

which is positive when $z=0$, and negative when $z=1$. Hence this again divides the pyramid by a single continuous diaphragm extending from B D, D A across to a point in O C;

and it must therefore cut the curve C E at one point, and only one.

24. That the equations possessed at least one set of solutions answering the given conditions, we might have known *à priori*, since the hypothesis is a possible one, and being a possible one, must have some real solution. But we could not assert beforehand that there could only be one; and this last result is most important, since it shows us that our hypothesis is not sufficient to account for the fact that a mixture of two gases may exist at the same temperature in two different states, as, for instance, N + O and NO. From *à priori* considerations we might have thought, as I stated in § 6*, that two such states could be possible. But, further, not only does it show that the particular hypothesis of dissociation we have used is incapable of explaining this fact, but it also leads us to conclude that no other, depending on mutual influence as affected by the motion of translation, is sufficient for the explanation.

25. If we consider fig. 1, we see that the reason why we can only have one suitable solution is that the surfaces cut O A, O B, ... in only one point. If, for instance, O A, B D were cut in two points, then we should get two solutions; if, in addition, O B and A D were cut in two points we should get four solutions; and if O C were also cut in two points we should get five solutions, and possibly eight. Hence, in order to have two solutions, one of the three lines O A, O B, O C must be cut in two points. A glance at the equations will show that this can only be the case if the A, B, and C molecules are formed each in more than one way. One way of obtaining this is to suppose that when two molecules impinge, the atoms sometimes interchange: thus, for example, when two molecules A A and B B impinge, the result afterwards may be two molecules of C; or when a molecule A A and an atom B impinge, the result may be an atom A and a molecule of C, &c. If we were to take this into account, our equations would then be of the form

$$\left.\begin{aligned} &a_{33}x'^2 + \mathrm{A}zx' + \mathrm{C}z^2 - \mathrm{L}xy' - x\{2a_{11}x + \ldots\} = 0, \\ &a_{44}y'^2 + \mathrm{B}zy' + \mathrm{C}z^2 - \mathrm{M}yx' - y\{a_{21}x + \ldots\} = 0, \\ &a_{34}x'y' + \mathrm{L}xy' + \mathrm{M}yx' - 2\mathrm{C}z^2 - \mathrm{A}zx' - \mathrm{B}zy' \\ &\qquad\qquad - z\{a_{01}x + \ldots\} = 0. \end{aligned}\right\}$$

But if we now treat these new equations in the same way as the former we shall find that we are no better off, and that we can get only one suitable solution.

26. Another modification of our hypothesis suggests itself.

* Phil. Mag. June 1877.

We know that the mean internal energy of the molecules is in a constant ratio to the energy of agitation; and it is also highly probable that when the internal energy of a particular molecule is greater than a certain quantity, the molecule can no longer exist. This would modify the distribution of the velocities slightly; but the number breaking up in any time from this cause will be expressed by the number of molecules existing multiplied by a coefficient which is a function of the temperature. This only adds to the equations terms of the form $-\lambda x$, $-\mu y$, $-\nu z$, and, as before, we shall only get one set of solutions. None of these hypotheses, then, accounts for more than one state of a gas at a given temperature. Is it possible that, as some think, the action between two atoms is alternately attractive and repulsive, and hence that collisions with blows between (say) c and c' make the molecule split up, those with blows between c' and c'' produce a combination, &c., where $c<c'<c''<\ldots$? It is probable that in this case two states of the gas at the same temperature may be possible; but the reactions appear too complicated and arbitrary to be consistent with the general simplicity of nature.

Any hypothesis which would allow us to write the first two equations in the form

$$a_{33}(\alpha-x')^2-x\{\ldots\}=0, \text{ \&c.},$$

where α is a positive function of the temperature $<\frac{1}{2}$, might allow two or more states, as is evident by putting $x=0$, $x=\alpha$, $x=\frac{1}{2}$ in succession, when the left-hand member becomes positive, negative, and possibly positive alternately. But I cannot see any physical justification for this form. We seem driven, then, to the conclusion that, though dissociation may exist to some extent at all temperatures, it is not sufficient to account for the fact that two gases may exist combined or uncombined at the same temperature. Some modification will therefore be necessary; but what, is not clear: most probably a combination of the three just suggested.

27. Whatever our hypothesis may be, not only will it be necessary that the solutions of our equations satisfy the relations in § 23, but they must be such that the resulting state of the gas is a stable one. It is necessary therefore to determine the conditions of stability. Suppose, after eliminating x' and y', that the equations are

$$\left.\begin{aligned}\frac{dx}{dt}&=f_1(x, y, z),\\ \frac{dy}{dt}&=f_2(x, y, z),\\ \frac{dz}{dt}&=f_3(x, y, z).\end{aligned}\right\}$$

To find the state of equilibrium of the gas, we must put

$$\frac{dx}{dt}=\frac{dy}{dt}=\frac{dz}{dt}=0.$$

Suppose x_1, y_1, z_1 one set of roots of the resulting equation. This will give a stable state to the gas if, when x_1, y_1, z_1 receive any small variations, the gas tends to return to its former state. Suppose that x_1, y_1, z_1 are disturbed to $x_1+\xi$, $y_1+\eta$, $z_1+\zeta$; then, by Taylor's theorem, since $f_1(x_1, y_1, z_1)=0$, &c.,

$$\left.\begin{aligned}\frac{d\xi}{dt}&=\frac{df_1}{dx_1}\xi+\frac{df_1}{dy_1}\eta+\frac{df_1}{dz_1},\\ \frac{d\eta}{dt}&=\frac{df_2}{dx_1}\xi+\quad .\quad .\quad .\quad .,\\ \frac{d\zeta}{dt}&=\frac{df_3}{dx_1}\xi+\quad .\quad .\quad .\quad .;\end{aligned}\right\}$$

and these equations must be such that ξ, η, ζ never become large, and ultimately vanish. To solve them we put

$$\xi=\alpha e^{\lambda t},\quad \eta=\beta e^{\lambda t},\quad \zeta=\gamma e^{\lambda t},$$

and obtain, in the ordinary way, to find λ, the equation

$$\left|\begin{matrix}\frac{df_1}{dx}-\lambda, & \frac{df_1}{dy} & \frac{df_1}{dz}\\ \frac{df_2}{dx}, & \frac{df_2}{dy}-\lambda, & \frac{df_2}{dz}\\ \frac{df_3}{dx}, & \frac{df_3}{dy}, & \frac{df_3}{dz}-\lambda\end{matrix}\right|=0.$$

This is a cubic; and we therefore get three values of λ, say λ_1, λ_2, λ_3. Whence

$$\xi=\alpha_1 e^{\lambda_1 t}+\alpha_2 e^{\lambda_2 t}+\alpha_3 e^{\lambda_3 t},\quad \eta=\ldots,\quad \zeta=\ldots.$$

There will be two cases, according as all the roots are real or two imaginary:—

I. All real. Here the single condition that ξ &c. may not increase is that λ_1, λ_2, λ_3 must all be negative.

II. One real (λ_1) and two imaginary ($\lambda\pm\mu i$). In this case

$$\xi=\alpha_1 e^{\lambda_1 t}+\alpha_2 e^{\lambda t}\cos(\mu t+\alpha_3),\quad \eta=\ldots,\quad \zeta=\ldots.$$

Here, then, λ_1 and λ must both be negative. Both cases are contained in the statement that the real part of the roots of the cubic must be negative.

The two cases belong to two totally different kinds of stability. In case I. the gas returns directly to its normal state, but only arrives exactly at it after an infinite time. In

case II. the gas returns to its normal state by oscillations through it, whose amplitude continually diminishes without limit.

28. As the temperature of the gas increases, the proportions vary in general continuously; so that, if two states are possible, the state at any time will depend on its previous history. If one set of solutions remains real and gives a stable state at all temperatures, we may call that a normal state of the gas. For instance, in the case of hydrogen and oxygen, that set which answers to the state of steam is the normal state: as the temperature increases, the proportions of water-vapour, hydrogen, and oxygen vary continuously and always give a stable state. On the other hand, that set which answers to the state $2\,H + O$ is not normal: as the temperature rises, the proportions vary continuously up to a certain temperature, when they produce an unstable state; and the gas changes abruptly into a more stable one, which may be a normal state or one whose point of instability is at a higher temperature.

Any non-normal state may change into a normal state; but a normal state cannot, by mere alteration of temperature without external influence, be changed into a non-normal one. For instance, steam may be heated up to a point where there is scarcely any proportion of $H_2\,O$, but if it be cooled back it will change continuously to its former state. If $2\,H + O$ be heated up to the same temperature, at a certain temperature we get a sudden change to the normal state of steam; then the proportions vary as in the former case, and as the temperature falls it does not pass back to its former state of $2\,H + O$. In order, therefore, to obtain a gas in a non-normal state we must bring some external influence to bear on it.

29. As the temperature increases, two sets of solutions may become equal. To which set will the gas belong as the temperature increases or decreases through this point? In general, if any disturbance occurs, such as increase of temperature, a certain time is required for the gas to adjust itself to its new conditions. Would that state be taken up which most quickly adjusts itself? In this case we may learn something from the stability-equation in § 27.

If two solutions become equal, then the intersection of two of the surfaces

$$f_1=(x, y, z)=0,\quad f_2(x, y, z)=0,\quad f_3(x, y, z)=0$$

must touch the third. Let x_1, y_1, z_1 be such a point; l, m, n the direction-cosines of intersection of f_1 and f_2. Then

$$l\frac{df_1}{dx}+m\frac{df_1}{dy}+n\frac{df_1}{dz}=0,$$

$$l\frac{df_2}{dx}+\quad .\quad .\quad .\quad =0;$$

also

$$l\frac{df_3}{dx}+\quad .\quad .\quad .\quad =0;$$

$$\therefore\ \begin{vmatrix} \frac{df_1}{dx}, & \frac{df_1}{dy}, & \frac{df_1}{dz} \\ \frac{df_2}{dx} & . & . \\ . & . & . \end{vmatrix} =0.$$

Hence we see that the stability-cubic is satisfied by $\lambda=0$; or for certain disturbances in the gas, it tends to retain them, and for those disturbances we must take into consideration quantities of the second degree.

30. If we could solve generally the equations in § 22, we should then be able to determine the relative effects of the radii of action and of the dissociation-temperatures on the resulting state of the compound. But all we can do is to give numerical values to the constants involved, determine the corresponding states in several typical cases, and infer general laws. This work is great, and the result scarcely worth the labour; but in one purely imaginary case the equations become simpler, viz. when the two component gases are mechanically similar. In this case I find, supposing $\theta_1=\theta_2=\frac{4}{5}\theta_0$, and $s_{33}=\frac{1}{\sqrt[3]{2}}s_1$, that $x=y$, $x'=y'$ gives the single suitable solution, and that the relations between x, z at different temperatures are given by the abscissæ and ordinates of the curve in fig. 2, the corresponding values of x' being $\sqrt{5}\times$ distance from A B. The curve outside O A B represents a set of unsuitable solutions in which x' is negative. From this the curves in fig. 3 have been laid down. The abscissæ represent the temperatures in terms of O E$=\theta_0$, the ordinates of A B the proportion of compound molecules to moving particles, and the ordinates of C D the proportion of moving particles to the whole number of atoms, O A being unity. It is noticeable that, as the temperature increases, the proportions of compound vary very slightly at very low temperatures, then vary very rapidly, and again very slowly at temperatures above θ_0. If $\theta_0=5000$, then at a temperature of 527° C. the proportion of compound is about $\frac{1}{2}$. It may also be noticed that x first

increases and then decreases, whilst z decreases and x' increases continually as the temperature rises, so that the gas has the same proportion of A or B at *two* temperatures. For this type of gas the stability-cubic is easily solved; for since

$$\frac{df_1}{dx}=\frac{df_2}{dy},\quad \frac{df_1}{dy}=\frac{df_2}{dx},\quad \frac{df_1}{dz}=\frac{df_2}{dz},\quad \frac{df_3}{dx}=\frac{df_3}{dy},$$

we may write the cubic in the form

$$\begin{vmatrix} \kappa-\lambda, & a, & b \\ a, & \kappa-\lambda, & b \\ c, & c, & \kappa'-\lambda \end{vmatrix} =0;$$

one root of which is

$$\lambda=\kappa-a=\frac{df_1}{dx}-\frac{df_2}{dx};$$

and the others are found by the quadratic

$$\begin{vmatrix} 1, & -1, & 0 \\ a, & \kappa-\lambda, & b \\ c, & c, & \kappa'-\lambda \end{vmatrix} =0.$$

It may be noticed that

$$\frac{df_1}{dx}-\frac{df_2}{dx}=-\{4a_{33}+2a_{13})x'+4a_{11}x+a_{10}z\},$$

and is therefore a negative quantity.

31. I have also worked out the case of a compound gas with a diatomic molecule, in which the masses of the components are nearly equal ($m_1=14$, $m_2=16$), the radii of action the same as those of $\overline{\mathrm{N\,N}}$, $\overline{\mathrm{O\,O}}$, and $\overline{\mathrm{N\,O}}$, and $\theta_1=\frac{4}{6}\theta_0$, $\theta_2=\frac{5}{6}\theta_0$. The results are exhibited by the curves in fig. 4. The thick black curve A B represents the relation between the numbers of compound molecules $\overline{\mathrm{A\,B}}$ and the temperature; the thin curves O C, O C′ give the numbers of $\overline{\mathrm{A\,A}}$ and $\overline{\mathrm{B\,B}}$ molecules respectively, and O D, O D′ those of the A and B atoms; in each case the dotted curve belongs to the B component.

These curves show us at a glance what happens as the temperature increases from zero. At zero the whole gas is in the compound state. As the temperature rises, at first very little dissociation takes place; and then a small proportion of the compound becomes gradually dissociated, but the dissociated atoms chiefly recombine at once to form A A and B B molecules. As the temperature still further increases to about $\frac{1}{4}\theta_0$, the dissociation of A B takes place very rapidly, most of its dissociated atoms now remaining so, but some still recombining to form A A and B B. At about $\frac{1}{6}\theta_0$ or $\frac{1}{4}\theta_1$ the number

of dissociated atoms and of molecules of A A and B B become equal. As the temperature still further rises, the numbers of molecules of A A and B B become a maximum somewhere about $\frac{1}{3}\theta_0$, after which they become less and less, whilst at a temperature near $\frac{1}{2}\theta_0$ the number of dissociated atoms of A or B is about equal to the number of molecules of A B. From this point the dissociation of A A, B B, and A B takes place pretty uniformly, until at an infinitely great temperature they cease to exist, whilst the number of A or B atoms increases correspondingly up to N.

32. The final conclusion we must draw is that an hypothesis which depends for the explanation of chemical combination on the dissociation of the component molecules, and combination of the dissociated atoms by any simple law of attraction, is not sufficient to account for all the phenomena; but it seems as if the action between two atoms must be a complicated one. It may easily be shown that, unless there be dissociation at *all* temperatures, the dissociation at high temperatures cannot be explained simply on the supposition that the internal energy of the molecule is too great to allow it to exist. For let Q_t, Q_0 be the heats of combination of two gases (masses m_1, m_2) at temperatures t and o respectively, c_1, c_2, c the specific heats at constant volume of the components and compound; then by combining the gases at temperature t, cooling the compound to zero, decomposing, and heating the mixed gases up again to temperature t, we may show that

$$Q_t = Q_0 - \{(m_1+m_2)c - m_1c_1 - m_2c_2\}t.$$

Now suppose t to be the temperature at which dissociation of the whole would suddenly take place, then clearly $Q_t = 0$, and we should have

$$t = \frac{Q_0}{(m_1+m_2)c - m_1c_1 - m_2c_2}.$$

In the case of a diatomic perfect gas, $c = c_1 = c_2$ and $t = \infty$; or no dissociation could take place unless $Q_0 = 0$, *i. e.* unless there is never any combination. But gases are only nearly perfect, and consequently the denominator in the above will be extremely small: *e. g.* if we take the case of H_2O, and suppose that the specific heats remain the same at all temperatures, we shall find that t has a value which must be greater than 64,000° C.; and we know that steam is almost wholly decomposed at temperatures far below this.

33. So much we gather as to the chemical properties of gases. The physical properties of simple elementary gases were discussed in the previous paper with a somewhat more

satisfactory result; though a mistake, pointed out in the July Number of this Journal, renders the reasoning less convincing. When the correction is made it will be found that the ratio of the specific heats, when $\theta_0 = 5000$, is not 1·4, but much smaller. For some value of θ_0 between 100° and 5000°, probably about 500°, the value of $\frac{c'}{c}$ will become 1·4; but then ζ will be something near ·4, and about three fifths of the gas will be in a state of dissociation. This we cannot allow; for though we might explain the near equality of the pressures and specific heats of different gases by supposing that θ_0 is the same, or nearly the same, for each, yet the constancy of the specific heats with respect to temperature will not now hold even approximately. The difficulty as to the ratio of the specific heats therefore still remains.

XXIII. *On an Apparatus to illustrate the Interference of two Plane Waves.* *By* C. J. Woodward, *B.Sc.**

THE effect produced by the simultaneous propagation of two or more plane waves is in a few simple cases easily realized; in others, however, the mind is somewhat harassed in ascertaining what will be the resultant wave made up of certain given elements. The apparatus I am about to describe is intended to assist the student by enabling him to draw for himself the required resultant wave; or the apparatus may be used in the class-room to illustrate the general subject of interference.

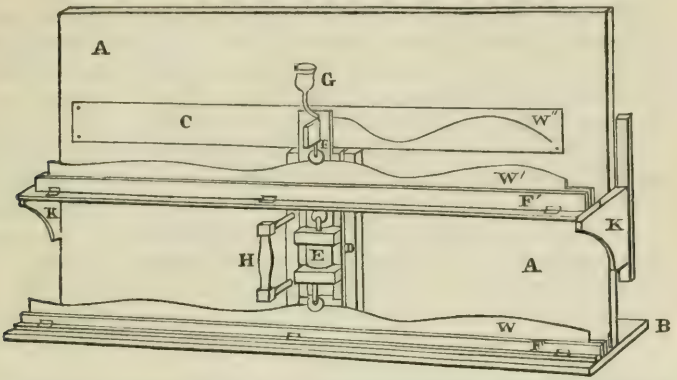
So far as I know, the only apparatus of the kind in use by lecturers is one based on the method described by Dr. Young (Natural Philosophy, Lecture xxxiii.); but here, to obtain any variety of effects, a series of dissected waves are required, and these are troublesome to make or expensive to purchase; whereas with the arrangement I now exhibit to the Society, when once the framework of the apparatus is made, combinations of any desired waves may be drawn, with merely the trouble incidental to cutting out the required waves in cardboard or thin tin.

The apparatus consists of a board, A A, about 3 feet long, 2 feet wide, and 1 inch thick, set upright on a base-board B. A strip of cardboard, C, is fastened by drawing-pins to the board; and on this is drawn the compound wave resulting from the two component waves W, W′. These component waves are cut out of strong cardboard or tin, and can be easily

* Communicated by the Physical Society.

and quickly placed in position by letting down the flaps F, F′. D is a stout mahogany board, with a wedge-shaped groove in

Fig. 1.



Moving the boards D, E, F from right to left by means of the handle H traces the wave W″, a combination of the waves W and W′.

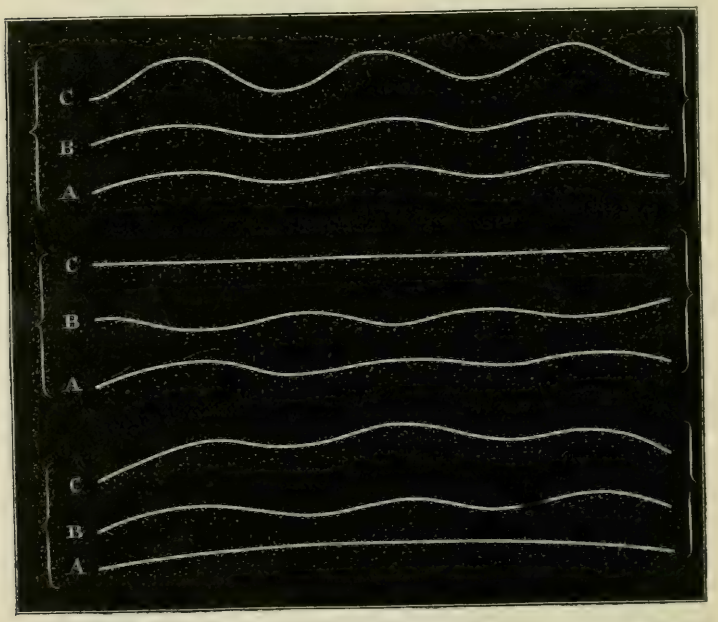
it sufficiently wide to allow the board E to slide freely up and down. A handle, H, is secured to the board D to enable the operator to move D from one end of A to the other. The board E has a pulley fastened to its lower part; and this pulley runs on the tin wave W, so that if the board D be moved horizontally, the sliding board E will rise and fall as the pulley passes over W ; and of course, were there a pencil attached directly to E, the pencil would trace a curve the same, or very nearly the same, as that of the wave. The sliding board E has also a wedge-shaped groove cut in it to allow the board F to slide vertically ; and to F is also attached a pulley, which runs on the wave W′. With the upper board F, as with the lower, if the pulley be made to traverse the wave W′, a pencil fastened to F would trace a wave corresponding to W′. The pencil (or, more properly, pen) used in the apparatus consists of a thistle-funnel, with the tube drawn out so as to have an opening of only a fraction of a millimetre. The tube is bent as shown in the figure at G ; and the drawn-out part presses gently against the cardboard C. To charge the pen, some violet ink is poured into the thistle-funnel, which is then closed with a cork.

The action of the apparatus will easily be understood. As the board D moves along, the board E rises and falls ; and this by means of a roller causes the wave W′ to rise and fall to each elevation and depression of the wave W below. Now

the board D as it moves along carries with it the sliding board F with the attached pencil; and as this board F is carried along it rises and falls to the elevations and depressions of the wave W′. But, as has been said, it also rises and falls to the wave W: the motion of the pencil is therefore the algebraic sum of the forms of waves W and W′. In the figure the waves W and W′ are of the same length and amplitude and correspond in phase, so that the tracing W″ is a wave of the same length but twice the amplitude of the waves below.

By moving the wave W′ to the right, its phase may be made $\frac{1}{4}$, $\frac{1}{2}$, &c. of an undulation different, and a fresh tracing obtained. By removing the wave W′ and inserting successively others of different lengths and amplitudes, various combined waves are traced out on moving the board D along. A few tracings obtained by the apparatus are represented in fig. 2.

Fig. 2.



The wave C results in each case from the superposition of the waves A and B immediately below C.

In order that the frame carrying the wave W′ may rise and fall freely, the brackets K, K are linked together at the back of the board by a parallel motion, used in the Cowper printing-

machine, and which will be found described in Goodeve's 'Elements of Mechanism,' 3rd edit. page 66.

It is obvious that by an extension of the same principle an apparatus could be made to give the tracing of a combination of three or more waves. To do this, however, the mechanical arrangements must be much better than in the comparatively rough instrument I have exhibited.

XXIV. *On Chemical Classification.* *By* M. M. Pattison Muir, *F.R.S.E., Assistant Lecturer on Chemistry, The Owens College, Manchester.*

[Continued from p. 99.]

18. FROM what has been said in the preceding paragraphs, it is apparent that to fix the valency of an element is a most difficult task. I think it is also apparent that at present it is only from gaseous compounds that we can look for much help in this task. So difficult is it to determine the valency of an elementary atom that many chemists have been inclined to regard each element as possessed of several valencies varying with the compounds which the element forms. Thus carbon in carbonous oxide would be regarded as a dyad, and in carbonic oxide or in marsh-gas as a tetrad. Other chemists have regarded the power of combining with a definite number of hydrogen, chlorine, &c. atoms as an essential and unalterable property of the elementary atom. To say that the atom of an element is now divalent, now trivalent, to attempt to *explain* the differences between compounds by means of the hypothesis of "varying valency" is, as Lothar Meyer has well pointed out, to vouchsafe no explanation at all. What is required from the upholders of the "varying-valency" theory is a reference of the different valencies exhibited by one and the same element to some distinct and definite cause. The question at issue is most distinctly stated in Meyer's work already referred to (2nd edit. pp. 244, 245), "Is every elementary atom capable of combining with a certain definite number of other atoms? and is this power solely dependent upon the nature of the matter composing the atom, or is it also conditioned by outward circumstances?"

The general facts, some of which have been enumerated in paragraphs 15, 16, and 17, appear to me to justify one in concluding that, probably, the capacity of saturation of each atom is an essential and definite property of the atom, dependent upon the nature of the matter composing the atom, but that this power is capable of being modified or conditioned by extraneous influences. Whether these extraneous influences are

capable of modifying the general action of the elementary atom, or whether they are capable of bringing about changes in the inner mechanism of the atom itself, in which case we should have an explanation of "varying valencies," must at present remain undecided. Summing up the evidence, Meyer asserts (and, it seems to me, truly asserts) that we are justified at present in regarding the "elementary atoms as fixed magnitudes, and the composition of compounds as deducible (1) from the unchanging valency of these atoms, and (2) from the changing circumstances under which this valency is exercised, or by which it is influenced in its working."

Besides most fairly, as I think, summing up the evidence, this statement of Meyer presents us with an admirable working hypothesis; it is especially valuable as a guide in the application of the principle of valency to chemical classification.

19. Granting, then, that each elementary atom possesses a certain capacity of saturation of its own, it would appear that the general nature of compound bodies must be in some way correlated with the valency of their constituent elements. Omitting for the present the consideration of the influence exerted upon the general nature of compounds by the changing circumstances under which their elementary atoms enter into combination, let us see whether it is possible to express the composition of some of these substances as a function of the valency of the combining atoms.

"Any quantity which depends upon and varies with another quantity may be called a function of it, and either may be considered a function of the other."*.

The problem may be stated in other words:—Can it be shown that the general chemical composition of a group of compounds varies with the valency of the elementary atoms composing these compounds? When the valency varies, does the composition vary with it?

The problem is an exceedingly difficult one to solve. In "valency" we have a measurable quantity; but where shall we find a unit in terms of which "general chemical composition" may be measured?

If problems of the kind under consideration are to be rigorously dealt with, it is necessary that the variable quantity should be under the control of the experimenter, and that he should be possessed of means for carrying out similar experiments under similar conditions. In the present instance valency is probably a fixed quantity; chemical composition is variable, but it is so ill-defined that we cannot be certain that

* W. Stanley Jevons, 'Principles of Science,' vol. ii. p. 113.

two experiments which appear to be carried out under similar conditions are really so carried out.

Nevertheless we may arrive at a conviction that these two quantities (valency and chemical composition) are really connected together, if we notice that "one always varies perceptibly at the same time as the other"*, although we may be unable accurately to measure the quantities, or to state the quantitative relations existing between them.

The only way of dealing with the question before us is, I think, to attack it in detail. We must endeavour to decompose the quantity "general chemical composition" into parts, and to establish a relation between each of these, in succession, and the valency of the elementary atoms. If this could be accomplished, the further problem would still demand solution, Does the simultaneous variation of several parts modify their separate actions?†

20. It would be beyond the limits of such a paper as the present to attempt any more than the briefest outline of the results which have been obtained in the attempted solution of the various parts of the problem under consideration. Starting with the hypothesis (shown on other grounds to be a probable hypothesis) that the valency of each elementary atom is a fixed quantity, it becomes possible to deduce the forms of combination of a stated number of different elementary atoms, the valency of each being given. The question is mainly a mathematical question‡, although the occurrence of unsaturated compounds &c. may complicate it. But the only means which we at present possess of assigning the probability to the results of such a deduction is, studying the general chemical and physical properties of the various compounds of the elements in question. From a certain assumption concerning valency we deduce a number of possible formulæ, each of which represents a definite compound; but we cannot lay our hand on this or that compound; we have no means of certainly identifying any one of the hypothetical compounds. Each of them may have been prepared and studied by us, and we may yet have failed to recognize any one of them. We make a second assumption, in favour of which there is indeed much evidence, viz. that the general characteristics of compounds are correlated with inner structure, or, in other words, with composition. From what we can actually observe of the general characteristics of the compounds of the given

* Principles of Science, vol. ii. p. 110.

† See 'Principles of Science,' vol. ii. p. 55.

‡ For a full discussion of this part of the problem see *Die modernen Theorien*, pp. 138–170.

elements, we attempt to measure the probability in favour of the second assumption; and from the probability so obtained we attempt further to measure the probability in favour of the first assumption *.

So far as the first links in this chain are concerned there is no great difficulty; given fixed valency, the possible combinations of a number of atoms are readily deduced; but when we come to deal with general characteristics and with chemical analogies, all is vague and unsusceptible of quantitative treatment. And then there comes the dread, "What if valency is not fixed? what if it is an essentially variable quantity?" And then we seek to allay the uneasy feeling by appeals to chemical analogies and general characteristics; and so we get into a circle and become entangled, and perhaps in despair seek refuge in those graphic formulæ and strange pictures which, like some religions, demand implicit assent from their victim, but promise him in return rest and quietness of mind.

I cannot help thinking that chemists sometimes fail to distinguish the kind of evidence upon which constitutional formulæ are based (but here again we may disagree as to the meanings to be assigned to the words "constitutional formulæ"), and that they are inclined to repose too much trust in these formulæ.

Some have rushed to the other extreme; they have, with that "infinite capability of doubting" which is said to be a characteristic of the "ideal reformer," refused to have dealings with the commonly accepted notions which connect together valency, structure, and properties, and have endeavoured to found upon a system of "dynamic equivalents" a more definitely quantitative classification of chemical substances. Their attempts are worthy of all success; but the task is a long and a laborious one. I can see no reason for not using both methods in the solution of the general problem of classification. However we may succeed in deducing dynamical equivalents, we cannot overlook the connexion which, it appears, *must* exist between composition and general action. "Composition," to quote the words of Professor Foster in the article "Classification" in Watts's 'Dictionary' (vol. i. p. 1022), "Composition is the most fundamental of all chemical properties; and the manner in which all other chemical properties depend upon it is the fundamental problem of Chemistry."

The upholders of the "position theory," it appears to me, recognize this truth, although sometimes the intensity of their

* No shadow of an attempt at the actual quantitative measurement of any of these probabilities has been, or can be as yet, attempted.

recognition has closed their eyes to other truths. Do not the upholders of what may be called the "energy theory" sometimes overlook the paramount importance of "composition"? Granting that "similarity of action is correlated with similarity of composition"*, how are we to measure the "action" of chemical compounds?

What I have to say of general chemical analogies as aiding us in answering this question I shall defer until I come to speak of Mendelejeff's periodic law. The physical properties of compounds present us with measurable quantities; and it seems to me that by measuring certain of these we have a means of arriving at a more definite knowledge concerning the relations existing between structure and chemical function.

21. In attempting to show that there is a connexion between the physical properties of compounds and their composition, as part of the wider problem of the connexion between chemical character and the valency of the combining atoms, I must content myself with the merest outline of the field of investigation.

In a paper on Isomerism, published in this Magazine (September 1876), I drew attention to the probable connexion existing between the boiling-points and the composition of groups of chemical compounds. Isomeric substances exhibit different boiling-points or different degrees of fluidity: we can scarcely do otherwise than attempt to correlate these with differences in structure; and in the paper cited I adduced examples to show that we have some evidence for such a correlation†. The melting-points of solid substances are also, in all probability, functions of the structure of these bodies. Few attempts have as yet been made towards systematizing the results of experiments upon melting-points; accurate and numerous data must be first obtained.

Most intimately connected with the boiling-points of liquids is the question of the vapour-tensions of these liquids. Every vapour exerts a certain pressure or tension, which is mainly dependent upon the temperature of the liquid. The upholders of the molecular theory of matter regard this tension as due to the motion of the molecules, to the striving of these molecules to escape into the less closely packed atmosphere surrounding them. The higher the temperature of the liquid the more rapid will be the movements of the molecules; the greater therefore will be the tension of the vapour. The tension of a vapour is a measurable quantity; it may be regarded as a variant, temperature being the variable. In order to trace the

* *Die modernen Theorien*, 2nd edit. p. 173.

† See H. Kopp, *Ann. Chem. Pharm.* xcvi. p. 2; Kekulé, *Lehr. der org. Chem.* i. p. 281 *et seq.*

connexion probably existing between the tension and the chemical composition of vapours, it would be necessary to determine the tensions of many groups of compounds at the same temperature, or, better still, to determine the connexion existing between tension and temperature for each compound throughout a considerable range. Meyer* has well pointed out the disadvantages of the usual practice, which is to determine the temperature at which each vapour exerts a tension equal to 760 millims. of mercury. There is no doubt that careful determinations of vapour-tensions of groups of compounds would throw much light upon the composition, and so upon the classification of these compounds †.

Connected with determinations of boiling-points and of vapour-tensions is the general question of specific and latent heat. We say that bodies have different capacities for heat, or that different quantities of heat must be communicated to equal masses of different bodies in order to produce equal increments of temperature in these bodies. Evidently part of the heat communicated has disappeared; and different proportions of the total heat have disappeared in each case. We have adopted a practical unit for measuring the amount of heat which has disappeared. We believe that this heat has gone to do work of some kind. Different amounts of work must be done in different elements and compounds before the heat added begins to be apparent to our measuring-instruments. There must surely be differences in the inner structure of these elements and compounds. May we not reasonably hope that careful determinations of those quantities which we call specific and latent heats, carried out for groups of compounds as they have been partly carried out for groups of elements, will throw considerable light upon the composition of these compounds?

In connexion with this subject we must look with much interest to the results of Weber's promised researches upon the specific heats of carbon compounds. From his preliminary researches, Weber thought himself justified in concluding that "the specific heat of carbon when in combination is a function of the temperature, and of all those circumstances which influence the quality of the non-carbonated part of the compound molecule"‡.

* *Die mod. Theor.* 2nd edit. pp. 203, 204.

† See H. Landolt, *Ann. Chem. Pharm.* Suppl. Bd. vi. p. 129.

My friend Mr. J. B. Hannay is now working at this question by an original method; he has already obtained good results.

‡ See translation, by the author, of Weber's paper, "On Specific Heats of Carbon, Boron, and Silicon," in this Magazine for April 1875, [IV.] vol. xlix. pp. 300–302.

Measurements of the diffusion, of the viscosity, and of the transpiration of liquids have already thrown some light upon the chemical composition, and so upon the classification, of these liquids.

"The coefficient of diffusion represents the rate at which the equalization of chemical composition goes on by the exchange of the molecules themselves." "The coefficient of viscosity . . . . represents the rate at which the equalization of velocity goes on by the exchange of the momentum of the molecules"*. In each case, "if the temperature remain the same, the rate of equalization is inversely proportional to the density"†. But the density is proportional to the mass of the molecules; hence heavy molecules will diffuse more slowly than lighter molecules. The velocity with which the molecules diffuse, or the velocity with which they pass through capillary tubes, will therefore be dependent upon the relative masses of those molecules; hence our knowledge of the molecular weights of solid and liquid compounds may be very materially advanced by careful measurements of the coefficients of diffusion, viscosity, and transpiration of various bodies. And if this be so, much light would be thrown by such researches upon the general problem of chemical classification‡. If from researches on diffusion, viscosity, and transpiration we may hope for determinations of the relative magnitudes of solid and liquid molecules, it is evident that such researches will also throw light upon the question of the chemical composition of mixtures of several compounds which are capable of exerting actions upon one another, but which remain, along with the products of their mutual actions, in a state of solution §.

Kopp‖ and others have established the fact that determinations of *specific* or *molecular volumes* throw much light upon the general composition of chemical compounds. The molecular volume of the compound is of course directly proportional to the molecular weight, and inversely proportional to the density. If we determine the molecular volumes of a series

* Clerk Maxwell, 'Theory of Heat,' 1st. edit. p. 302.

† Clerk Maxwell, *loc. cit.*

‡ See Graham's Classic Series of Researches; also Loschmidt, *Wien. Akad. Ber.* [2] lxi. p. 367 &c.; also in *Jahresber.* 1870, p. 58; also Wretschko, *Wien. Akad. Ber.* [2] lxii. p. 575 &c.; also in *Jahresber.* 1871, p. 51: Maxwell, Phil. Mag. [IV.] vol. xlvi. p. 468; Gueront, *Comptes Rendus,* lxxxiii. p. 1291; &c. &c.

§ Mr. Hannay is also engaged in investigating the problems presented by transpiration, or, as he prefers to call it, microrheosis of liquids. His method is wonderfully exact.

‖ *Ann. Chem. Pharm.* xcvi. pp. 153, 303; c. p. 91 &c.

of compounds whose molecular weights and densities are known, and if we can establish a connexion, admitting of exact expression, between these three quantities, then, when we meet with a new compound which appears from general analogies to belong to the group in question, the mere determination of its density may aid us materially in fixing the molecular weight and, generally, in classifying the compound.

Further, Kopp's researches show that there is a connexion between the structure of analogous compounds and their molecular or specific volumes. Determinations of the molecular volumes of series of analogous compounds, if very carefully made, must evidently be of the greatest assistance to the chemist who is attempting to reduce to some kind of order the immense array of imperfectly examined compounds accumulated by the industry of his fellow workers. In the course of determinations of molecular volumes, various valuable data bearing more or less directly upon the main question are also accumulated.

For these and other reasons chemists most anxiously expect the publication of that series of researches upon which Thorpe has been engaged for some years and which is now approaching completion.

The researches of Gladstone*, of Landolt†, and of others most clearly indicate that a connexion exists between the chemical composition of compounds and their action upon light. We have groups of terpenes most clearly marked off from each other, on the one hand by differences in molecular weight, on the other by differences in refractive indices, in dispersion, in sensitiveness, and so on. We have other bodies, often having the same molecular weights and the same empirical formulæ, but differentiated by the action exerted by them on a ray of polarized light. Can we doubt that structure and action on light are connected together in some way?

Lastly, I would refer to the connexion which undoubtedly exists between chemical composition and the thermal phenomena exhibited during the formation and decomposition of groups of compounds. When soluble hydroxides are neutralized by addition of sulphuric, hydrochloric, or nitric acid, the amount of heat evolved is almost the same in each case. When mixtures of acids are presented, in the proportions expressed by the molecular weights, to the same hydroxide, the thermal disturbances which ensue show that the hydroxide divides itself between the two acids in a definite manner. From a study of such thermochemical reactions, we are able to draw conclu-

* Chem. Soc. Journ. [2] vol. viii. pp. 101, 147, [2] vol. x. p. 1 &c.

† Pogg. *Ann.* cxxiii. p. 603.

sions regarding the comparative avidity of different acids for the same base*; and when these studies shall have been extended and generalized, we shall most probably be able to connect together chemical action and chemical composition. Questions concerning composition which appear almost incapable of solution by the ordinary method of reactions are even now beginning to be solved by the thermochemical method†.

But I cannot pursue this part of the subject further. I would only allude to the results obtained by Tyndall‡ as establishing a connexion between absorptive power of gases for heat and chemical composition; to the experiments of Rüdorff §, as pointing to a distinct connexion between lowering of temperature during solution of salts in water and the molecular weights of these salts; and to Guthrie's researches on "Salt Solutions and Attached Water"‖. The experiments of Gamgee upon the poisonous activity of ortho-, meta-, and pyrophosphoric acids, communicated to the Glasgow Meeting of the British Association, point to a connexion between chemical structure and physiological action.

22. The results of those experiments which have already been made upon the physical properties of groups of compounds justify us in concluding that there is a close connexion between these properties and the chemical composition of the compounds. To render this connexion more definite, to exhibit it as a quantitative connexion, will be one of the future triumphs of chemical science.

Assuming a certain valency for a given number of elements, we are able to deduce a number of possible formulæ for the compounds produced by the union of these elements. Many of these possible compounds have the same empirical formula. By actual examination we find that many compounds really exist each having that empirical formula which has been theoretically deduced; but we are able, from a study of the physical properties of these compounds, to say that they are really distinct bodies; we are able further to trace somewhat regular gradations of physical properties among them; it may be that we are able to prepare the complete series of isomeric compounds as laid down by theory, and to arrange them in a connected group, or groups, the members of which exhibit definite relations of physical

* See article "Chemistry," by Armstrong, *Encyclop. Brit.* 9th edit. p. 489 &c.

† For an example of the application of this method see the article referred to (pp. 497, 498), where the composition of periodic acid is discussed.

‡ Contributions to Molecular Physics, pp. 69–144.

§ Pogg. *Ann.* vol. cxiv. p. 62; vol. cxvi. p. 55.

‖ Phil. Mag. [V.] vol. i. pp. 354, 446; vol. ii. p. 213.

properties. If we can do this, we have very strong evidence (1) of the existence of an essential connexion between structure and physical properties, and (2) in favour of the hypothesis of valency as a foundation on which to build a general scheme of chemical classification. As a matter of fact, chemists have not yet succeeded in completing the chemical history of any group of isomeric bodies; but I think that the recent advances made in this direction warrant us in expecting that the history of many groups will be thus completed—that to do this is indeed a possibility, and that meanwhile to accept the hypothesis of valency, *as an hypothesis*, is not to overstep the limits of true scientific method.

Again, given two or more elementary atoms, and given the valency of these atoms, the existence of certain compounds becomes, theoretically, impossible. Every failure, succeeding honest attempts, to prepare these bodies lends strength to the theory. We have instances of such failures.

It also becomes possible, on the assumption that the valencies of the constituent atoms of a compound are known, to deduce the (theoretical) possibility or impossibility of the occurrence of certain reactions. It may be possible, we argue, to introduce a fresh atom of a certain valency into this compound; or we say the introduction of an atom of this valency must cause decomposition,—the compound, under the new condition of affairs, can no longer exist. Every experimental confirmation of such deductions is a point in favour of the theory. Are we not continually meeting with experimental confirmation of facts deduced from the theory of valency?

In attempting to deduce possible reactions &c. from the theory of valency, and in attempting to confirm these deductions by appeal to experiment and observation, it is essential that we bear in mind how very imperfect our theory as yet is. If we attempt to apply it to solid and liquid bodies, we find ourselves surrounded by contradictions and difficulties innumerable: we know almost nothing of the circumstances which condition valency. We are ever ready to draw sweeping conclusions utterly unjustified by the theory; we are prone to set up what might be called theoretical theories, vague, shifting, indefinite; and then, when the experimental evidence contradicts our deductions, we are liable to fall into one of two errors—either to manufacture a new, more vague, and more elastic theory to suit the results, or to doubt the utility of theory altogether. To use an hypothesis without abusing it is one mark of a master mind.

23. But in endeavouring to discover the relations which we assume to exist between valency and chemical composition, it

is necessary to fix our attention upon the chemical properties no less than upon the physical properties of groups of compounds. Assuming the hypothesis of valency, and given a certain number of elementary atoms and the valencies of these atoms, we deduce the possible existence of a group of compounds. Have we any chemical means for recognizing the existence of these compounds? From a study of the chemical processes involved in the formation, in the reactions, and in the decompositions of a group of bodies, can we gain any insight into the structure of these bodies?

Now, granting that there is some kind of structure, we may safely assume that difference in structure is correlated with difference in chemical behaviour. From a study of chemical behaviour we should then arrive at a knowledge of the structure of the bodies under consideration. Let us take an example. Analysis and vapour-density determinations point to the formula C_2H_6O as expressing the empirical composition and molecular weight of common alcohol. From the theory of valency (the valencies of the constituent elements being C^{iv}, H', and O'') we deduce the possibility of the existence of two compounds, each having the empirical formula C_2H_6O: for one of these we have the constitutional formula $CH_3—CH_2—O—H$, for the other the formula $CH_3—O—CH_3$. Which constitutional formula is to be assigned to alcohol? When alcohol is acted upon by sodium or potassium, one atom of hydrogen is exchanged for one of metal; the remaining five atoms of hydrogen cannot be so exchanged: it is also possible to substitute a monovalent group for one of the hydrogen atoms in alcohol. From the constitutional formula $CH_3—CH_2—O—H$, we should infer that one of the hydrogen atoms would be ready to undergo reactions which would not affect the remaining five. The formula $CH_3—O—CH_3$ points to no such difference between the atoms of hydrogen. Further, the first formula represents the sixth atom of hydrogen as alone in direct combination with oxygen: those substances which readily replace one atom of hydrogen in alcohol are themselves ready to combine with oxygen. Other reactions are known in which a monovalent group or element replaces the whole of the oxygen and simultaneously one atom of hydrogen in alcohol: thus,

$$C_2H_6O + HCl = C_2H_5Cl + H_2O,$$

$$C_2H_6O + HNO_3 = C_2H_5NO_3 + H_2O.$$

The possibility of such reactions is evident if we adopt for alcohol the constitutional formula $CH_3—CH_2—O—H$. But the product of the first reaction formulated above, C_2H_5Cl,

can have (according to our theory) but one constitutional formula, viz. $CH_3—CH_2Cl$. Inasmuch as this body has been produced by removing OH and putting Cl in its place, we conclude that the position originally occupied by the OH group was the same as that now occupied by the Cl*.

The reactions of alcohol then lead us to adopt the constitutional formula $CH_3—CH_2—O—H$ for this body. We know of another compound, viz. methylic ether, having the same empirical formula as alcohol: the general reactions of this compound point to the constitutional formula $CH_3—O—CH_3$. These two forms of the formula C_2H_6O exhaust the list of possible modifications deduced from the valency of the constituent atoms. We actually know of but two bodies having the empirical formula C_2H_6O.

What is the constitutional formula of acetic acid, $C_2H_4O_2$? Theory points to the possibility of the existence of unsaturated compounds, with two free affinities, having this empirical formula. Inasmuch, however, as acetic acid shows no tendency to form additive compounds, inasmuch as fresh atoms can only be caused to enter the molecule by substitution, it probably does not belong to the group of unsaturated compounds. Ten isomers of the formula $C_2H_4O_2$, all of them saturated compounds, are theoretically possible: two have actually been prepared, viz. acetic acid and the methylic ether of formic acid.

Acetic acid may be prepared from common alcohol by oxidation, two hydrogen atoms being replaced by one oxygen atom. But we have seen that the constitutional formula of common alcohol is almost certainly $CH_3—CH_2—O—H$. When this molecule is oxidized to acetic acid, which hydrogen atoms are replaced by oxygen? The H in the OH group is in all probability not replaced. The chief reasons for this statement are the facts:—that acetic acid, like alcohol, readily parts with one atom of hydrogen, and with one atom only, in exchange for metal, or for hydrocarbon radicles such as CH_3, C_2H_5, &c.; and that acetic acid and alcohol are evidently of very similar constitution, as is shown by such reactions as these:—

$$C_2H_6O + PCl_5 = C_2H_5Cl + POCl_3 + HCl.$$
$$C_2H_4O_2 + PCl_5 = C_2H_3OCl + POCl_3 + HCl.$$

If alcohol be represented by the formula $C_2H_5(OH)$, acetic acid may be represented by a formula constructed on the same

* The compound produced by the action of chlorine upon C_2H_6, viz. C_2H_5Cl, has been shown by Schorlemmer to be identical with the chlorine compound obtained from alcohol by the reaction formulated above.

type, viz. $C_2H_3O(OH)$. But in many reactions acetic acid splits up more completely than in those already enumerated. When an acetate is heated with an alkali-hydrate, methane is produced along with carbonate of the alkali; that is, one half of the carbon in the acetate passes away as gas in combination with the whole of the hydrogen, while the other half enters into combination with the whole of the oxygen, and with the whole of the metal both of the acetate and of the hydrate. The possibility of such a reaction is rendered apparent by adopting the constitutional formula $CH_3—CO—O—H$ for acetic acid. Other reactions of acetic acid also find their explanation in this formula, thus:—

$$CH_3—CO—O—Na + NaO—H = CH_4 + NaO—CO—NaO,$$

$$CH_3—CO—O—Na + NaO—CO—H = \underset{\text{Aldehyde.}}{CH_3—CO—H} + NaO—CO—NaO,$$

Sodium formate.

$$CH_3—CO—O—Na + NaO—CO—CH_3 = \underset{\text{Acetone.}}{CH_3—CO—CH_3} + NaO—CO—NaO.$$

In certain cases we are able to trace a connexion between the results deduced from such purely chemical considerations as those enumerated above, and the results of experiments upon the physical properties of a group of related compounds *. In my paper on Isomerism † I have endeavoured (par. 5) to show that a regular alteration in the boiling-points of the four butylic alcohols is correlated with a regular alteration in molecular structure. The constitutional formulæ there given to the four alcohols are obtained by a process of reasoning on *chemical* data similar to that illustrated in the cases of alcohol and acetic acid.

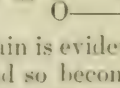
In endeavouring, therefore, to construct a constitutional formula attention should be paid to the physical properties as well as to the chemical reactions of formation and decomposition of the body to be formulated. Until, however, much more extended observations on the physical properties of groups of compounds have been carried out, the chemical method of arriving at constitutional formulæ must be regarded as the more important.

24. What I have called the chemical method of ascertaining

* For a fuller discussion of these and of other examples, see *Die modernen Theorien*, 2nd edit. pp. 176–192.

† This Magazine, September 1876.

the constitutional formula of a compound is based upon the hypothesis of valency and upon the hypothesis of atom-linking, which is itself an outcome of the former hypothesis. The idea of atom-linking has gradually arisen in chemistry; it is based more immediately upon the theory of types as interpreted in the light of the general theory of valency. From the vague ideas entertained in the earlier days of the atomic theory concerning the manner in which the atoms in a compound mutually influence one another, we have gradually advanced to clearer conceptions of atomic action. We now regard each atom in a compound molecule as exerting an action of some kind upon that atom, or upon those atoms situated near itself; we look upon chemical action as an action between atom and atom; we imagine a regular atomic system of some kind, not a conglomeration of atoms confusedly huddled together. We have attained to the notion of atomic "chains" and atomic "rings"* &c.

Most chemists now regard the molecule as an atomic system the members of which act and react upon one another in accordance with definite laws. The system is regarded as bound together in one whole, each part depending immediately upon the part next itself, and each depending mediately upon every other. From this idea, and from the theory of valency, the possibility of the existence of various kinds of atomic structures is deduced. For instance, a series of divalent atoms is capable of combining in two ways, either to form a "chain," such as —O—S—O—, in which case the molecule is evidently unsaturated, or to form a "ring," such as  , in which case the molecule is saturated. The chain is evidently capable of taking up two monovalent atoms, and so becoming a saturated molecule although still maintaining its "chain" character: thus we know of the compound SO_2Cl_2, which is probably constructed thus: Cl—O—S—O—Cl.

Constitutional formulæ are, then, based upon the theory of valency and the theory of atom-linking†. In determining these formulæ, certain subsidiary assumptions are generally made. Of these, perhaps the most important are the as-

* Of course we cannot for a moment regard the atoms in a molecule as fixed immovably in certain positions; we must look on them as in a continual state of motion. But this is not opposed to the idea of the maintenance of definite relative positions by the moving atoms.

† This statement may be denied by those who use the expression "constitutional formula" in a sense different from that in which I am now employing it. See forward.

sumptions:—(1) that the atoms constituting a group which makes its escape from a molecule during the decomposition of the latter existed in immediate combination with one another in the molecule; (2) that if a group of atoms can be caused to pass from one molecule into another, the constitution or structure of the group is not, as a rule, thereby altered; and (3) that if an atom or group of atoms be replaced by another atom or group of atoms of equal valency, the replacing atom or group occupies the place formerly occupied by the atom or group which has been replaced*.

These assumptions appear to be often verified by facts. Whether we are wholly justified in making them cannot be settled until extended researches upon the chemical analogies, and more especially upon the physical properties, of groups of compounds have thrown light upon the connexion which exists between chemical composition and the properties of chemical compounds. At present the assumptions may be looked upon in the light of working hypotheses.

I have frequently used the expression constitutional formula. It is necessary to define these words.

In a former paper† I have defined a constitutional or structural formula as a formula which "generalizes the reactions of formation and of decomposition" exhibited by the compound formulated. In another paper‡ I have insisted upon the advantages gained by the use of these formulæ as expressing "in the shortest possible manner the greatest amount of information about the actions of the substances formulated."

Now some chemists would, I think, be content to use constitutional formulæ, attaching to them some such meaning as that which I have just mentioned, while they would not be at all willing to accept the general theories of valency and of atom-linking; in fact, they might refuse to accept the atomic theory itself. But while I regard constitutional formulæ as doing all which I have claimed for them in the passages quoted above, I cannot but think that they also do something more. Accepting the theory of valency, imperfectly understood though it be, accepting the theory of atom-linking, both merely as hypotheses, and being fully convinced that a connexion between structure and properties really exists, I cannot regard constitutional formulæ as less than attempts to exhibit, so far as can be at present exhibited, that connexion. A constitutional formula generalizes facts concerning reactions of formation and of decomposition; it tells us much

* See *Die modernen Theorien*, 2nd edit. pp. 172, 173.

† "Isomerism," this Magazine, *loc. cit.*

‡ "On Chemical Notation," this Magazine, July 1876.

about the *doings* of the body formulated; and it attempts to connect those properties which it generalizes with the structure or composition of the chemical molecule. Attempts were made from the time of Berzelius to indicate by a formula something of the inner structure of the molecule. It is, however, only since we gained the idea of the molecule as a definite atomic system, each part depending upon each other, that these attempts have met with any fair measure of success.

In paragraph 20 of the present paper I have endeavoured to point out the difficulties in the way of certainly recognizing those compounds, the existence of which is possible according to the theory of valency. These difficulties hold in the present case. Compounds of this or that structure are theoretically possible; or this or that constitutional formula may be assigned to a certain compound; but how are we to tell what is the structure of the compound before us? How are we to make sure that the constitutional formula we adopt is the true one? We cannot tell; we cannot make sure. Like other scientific questions, this is a question of probability alone. And I think that the advances made by Chemistry, and more especially by the chemistry of the carbon compounds, in recent years, are the best proof we can have in favour of those hypotheses upon which our constitutional formulæ are based.

It is very well to insist upon the dangers of undue theorizing, and upon the necessity of amassing facts. Facts alone are of little use except as the foundations upon which true knowledge is raised. Is it not more scientific to venture an hypothesis, once we have accumulated a considerable mass of facts, and to use that hypothesis, than to remain contented with mere empirical knowledge? But all depends upon *how* we use the hypothesis. If we allow it to carry us away—if, for instance, in framing constitutional formulæ, we forget carefully to gather facts concerning reactions, or if we forget the limits within which it is alone allowable at present to make use of the theories of valency and of atom-linking, even of the theory of molecular structure itself—then in place of true constitutional formulæ we produce only "pictures" which are worse than meaningless, inasmuch as the information which they convey is in all probability false information, while the knowledge assumed on the part of those who manufacture them is certainly not as yet possessed by any human being.

25. In paragraph 4 of this paper I stated that the various systems of classification which have from time to time been triumphant in Chemistry might be broadly divided into two groups—those in which classification of chemical substances

was based upon the *functions* performed by these substances, and those in which the system was based upon the *composition* of the substances classified. In the six subsequent paragraphs I endeavoured to establish the truth of this statement upon historical evidence, while at the same time I attempted briefly to trace the rise of that system of classification which, founded mainly upon the doctrine of valency, should pay regard alike to function and composition in attempting to frame an exhaustive classification of chemical substances. In paragraphs 11 to 23 I endeavoured to sketch the outlines of the theory of valency, noticing the difficulties which have been overcome and those which are yet to be conquered; and I sought to show that a connexion really exists between the properties (chemical and physical) of a compound and the valency of its constituent atoms. I have also endeavoured to prove that the theory of valency, along with those subsidiary theories which have sprung from it, enables us to learn something concerning the composition or structure of chemical compounds. The facts already stated are, I think, a justification of what I said in paragraph 11, viz. that the system of classification which is mainly based upon the valency of the combining atoms pays regard alike to function and to composition of compounds. But I think it will now be possible to indicate in a more definite manner how this result is gained.

26. In paragraph 23 I have adduced reasons for assigning to common alcohol the constitutional formula $CH_3—CH_2—OH$, and to acetic acid the formula $CH_3—CO—OH$. One of the reasons given is the fact that one hydrogen atom, and one only, can be replaced by metal in either of these compounds. It is hardly correct to say, can be replaced by metal; for although the statement holds good, so far as we know, for acetic acid, yet it is only the alkali-metals which are capable of replacing one sixth of the hydrogen contained in alcohol; and, moreover, the alkali-metal must be presented in the isolated state. Although, then, we assign to each of the compounds under consideration a constitutional formula containing the group OH, yet we must believe that the function of this group is influenced in some way by the other atoms constituting the molecule.

From a consideration of the reactions of water, caustic potash, and hypochlorous acid, we assign to these bodies the formulæ H—OH, K—OH, and Cl—OH respectively; that is, we believe that the molecule of each contains the group OH: yet the properties of these three bodies are very different. It is impossible, on the theory of atom-linking, and accepting the generally received valency of the constituent atoms, to assign

to these compounds any other formulæ than those given above. The differences in the properties of these substances cannot, therefore, be accounted for by differences in structure; they must be dependent upon the nature of the constituent atoms other than oxygen and hydrogen. But we know of bodies possessed of the same empirical formula and of the same molecular weight as acetic acid, yet differing altogether in properties from this compound; these differences in properties are most probably due to differences in structure. If this view be accepted, it follows that just as differences in the nature of the atoms in a series of molecules, each containing the group OH, may cause this group to assume different functions, so differences in the structure of such molecules may produce a similar effect. Now the constitutional formulæ already assigned to alcohol and acetic acid exhibit differences in the structures of the two molecules*. In alcohol we have the OH group joined to the group CH_2 (CH_3—CH_2—OH); in acetic acid the OH group is joined to the group CO (CH_3—CO—OH). I have already detailed some of the reasons for adopting these constitutional formulæ. These two compound groups —CH_2—OH and —CO—OH are believed to exist in certain classes of alcohols and in acids respectively. Granting that carbon acids contain the group —CO—OH, it becomes possible very readily to determine the constitutional formulæ of many acids. Thus formic acid, H_2CO_2, can have (on our theory) but one constitutional formula, viz. H—CO—OH. There are many reactions by which we may recognize the compound groups —CH_2—OH and —CO—OH: the action of PCl_5, with the subsequent action of water upon the body produced, is one of the best; the action of the haloid acids is another; the action of the alkali-metals, contrasted with that of the alkalies, is a third; the action of methyl or ethyl iodide upon the metallic derivatives of the body under consideration, combined with the action of potash or ammonia upon the product so obtained, is a fourth. There are many other reactions.

We find that compounds containing the group —CH_2—OH yield, on oxidation, acids containing the group —CO—OH; but we have reasons for regarding the first group as characteristic of alcohols: some bodies which, for other reasons, must be classed among the alcohols, do not yield such oxidation-products as we should expect to be produced from substances containing the group —CH_2—OH. Such a result naturally leads to a further study of the apparently anomalous alcohols;

* Although these bodies are not isomeric, they may nevertheless be used as illustrations.

and we find that a second class of these bodies may be best regarded as containing a new group —CH—OH. For instance, we have primary butylic alcohol with the constitutional formula $CH_3—CH_2—CH_2—CH_2—OH$; but we have also secondary butylic alcohol with the constitutional formula $CH_3—CH_2—\underset{\displaystyle OH}{\underset{|}{CH}}—CH_3$. If the latter alcohol really contain the group —CH—OH, we are compelled to regard the position of this group as different from that assigned to the group $—CH_2—OH$ in the primary alcohol. Chemists speak of the OH as placed "at the end of the chain" in one case, and in the "centre of the chain" in the other.

Such ideas as these, founded on the theory of valency, developed by that of atom-linking, and, I think, in keeping with the reactions of the bodies to be formulated, compel us to believe that the action of each atom in a molecule is exerted, to a certain extent, upon all the other atoms; that just as in the planetary system we have a regular order of bodies, each occupying its own position and performing its own proper movements, yet each influencing and perturbing every other, so in a chemical molecule we have a group of atoms regularly arranged, each performing fixed and definite vibrations, each occupying a definite relative position, yet each exerting some influence upon every one and upon all of the remaining atoms*.

Such views as these are an outcome of the theories of valency and of atom-linking: they have led to many discoveries in chemistry in the past, and probably will be of yet greater importance in the future. In using them, however, it is very necessary to remember the small amount of knowledge which we really possess concerning the connexion existing between structure and chemical properties. Having gained the general idea of such a connexion, and finding that from what we know, or think we know, we can explain a considerable number of facts, we are ever ready to apply the explanations found to suit a few cases to every case, and so we come to imagine that our knowledge is practically complete.

For this reason, although I think that constitutional formulæ are one of the greatest aids which the chemist can possess himself of in his investigations, yet I also think that these formulæ must be carefully employed—that it is necessary for the chemist ever to remind himself that he is dealing with an hypothesis only, and with an hypothesis which is as yet but in the first stages of its development. The indiscriminate use of such expres-

* In the paper already cited I have endeavoured to trace the bearing of this view of the molecule upon the general theory of isomerism.

sions as "attached to a carbon atom at the end of the chain," &c. &c., especially in text-books for students (who generally find it hard to distinguish fact from theory), and unaccompanied by any warning, or explanation of the real value of the expressions, is, I think, much to be deprecated. It behoves us ever to bear in mind that in science we deal with phenomena made up of an infinite number of infinitely small units, and that therefore any deficiency in careful measurement may lead to the supposition of a causal connexion where no such connexion exists, that even at the best we gain only approximations, and that from the most carefully conducted experiments we cannot tell what may happen in extreme cases (Principles of Science)*.

[To be continued.]

XXV. *On some Dynamical Conditions applicable to* Le Sage's *Theory of Gravitation. By* S. Tolver Preston†.

1. THE tendency of modern science is undoubtedly to look to the existence of physical conditions or processes in those natural phenomena to which the theory of "action at a distance" has been applied. The gravitation theory of Le Sage has therefore of late naturally received a considerable share of attention. Le Sage finds it necessary, as a basis to his theory, to lay down certain conditions, some of which cannot but be regarded as arbitrary. Thus (as given in the paper by Sir William Thomson, 'Philosophical Magazine,' May 1873) Le Sage assumes among other conditions:—

(1) That the *direction* of the streams of particles producing gravity is such that an *equal* number of particles are moving in *all* directions.

(2) That the streams are all *equally dense*; or the total assemblage of matter forming the streams is of the *same* density in *all* parts.

(3) That the *mean velocity* of the streams is everywhere the *same*.

2. These conditions cannot but be considered arbitrary. My object is to call attention to the fact (which, if it has been observed, would certainly appear to be deserving of more attention than it has received) that all these conditions which Le Sage, with the limited knowledge of his day, assumed to be arbitrary, are in reality inevitable deductions following

* For a fuller discussion of the constitutional formulæ of alcohols and acids &c., see *Die modernen Theorien*, 2nd edit. pp. 190–202.

† Communicated by the Author.

from the dynamical principles connected with the kinetic theory of gases, or that Le Sage unconsciously enunciated the inevitable principles of the kinetic theory—that, in short, all the conditions laid down in Le Sage's theory are perfectly satisfied by a gas whose particles are very minute, and consequently the mean length of path of whose particles is very great. In other words, it may be stated as a general proposition, that when two bodies are immersed in a gas at a less distance apart than the mean length of path of the particles of the gas, the two bodies will tend to be urged together. Thus all the arbitrary conditions of Le Sage's theory (and all the facts of gravity) would follow as inevitable deductions from the simple fundamental admission of the existence of matter in space, whose normal state is a state of motion.

3. The part of Le Sage's theory which most calls for explanation, and which he makes no attempt to explain, is (even if we allow as a purely arbitrary fact that the motion of his particles took place at one time uniformly or *equally* towards all directions) how this uniformity of motion of the particles could be kept up under the continual changes of direction resulting from the collisions of the particles against themselves and mundane matter. Now it has been proved mathematically by Professor Maxwell, in connexion with the kinetic theory of gases, that a self-acting adjustment goes on among a system of bodies or particles in free collision, such that the particles are caused to move *equally* towards *all* directions, this being the condition requisite to produce equilibrium of pressure. The method of calculating the rate of the above self-acting adjustment for any case is given in the Philosophical Transactions for 1866. This adjustment is of such a rigid character that, if by any artificial means the motions of the particles were interfered with and made to take place irregularly (*i. e.* unequally in different directions), the particles when left to themselves would in a very short time automatically return back to the above *regular* form of motion, *i. e.* so that an equal number of particles are moving in any two opposite directions. Thus it follows that when a system of particles are left in space with nothing to guide them, they will, by the rigid principles of dynamics adjust their motions in such a way as to be competent to produce the effects of gravity. In other words, the movement of streams of particles with perfect uniformity at all angles (which Le Sage assumed as a mere arbitrary postulate) is found to be the necessary consequence of dynamical principles; or the particles themselves adjust their motions so as to move in uniform streams in all directions; and, further, when any disturbance of the unifor-

mity of the motion of the particles takes place due to their collisions with mundane matter, the particles themselves readjust the uniformity of motion.

4. Le Sage imagined that the collisions of the particles disturbed permanently the uniformity of their motions, and therefore supposed these collisions to take place only at intervals of time very remote from each other. Thus he assumes "....that not more than one out of every hundred of the particles meets another during several thousands of years; so that the uniformity of their motions is scarcely ever disturbed sensibly." We now know that, so far from the collisions of the particles among themselves disturbing the uniformity of their motions, this is the very cause which corrects and maintains the uniformity of motion, or preserves the uniformity of motion in opposition to external disturbing causes. The assumption, therefore, of the above enormous interval of time between the collisions of the particles, though admissible, is by no means necessary. The only necessary condition is that the path of the particle should be a certain *length*, not that a certain time should be occupied in traversing it. The time taken by the particle in traversing its path depends on its velocity; and this time might therefore be small, provided, under the conditions of the case, the velocity of the particle were high. Le Sage imagined that the collisions were detrimental, not only in destroying the uniformity of the motion of the particles, but also in destroying *vis viva*; and he therefore supposed the collisions to take place as seldom as possible. This belief in the destruction of *vis viva* at collision was universal at the time of Le Sage; and he therefore assumed that the gravific particles would finally come to rest, and gravity cease to exist. We now know that this is an error, and that motion is as naturally maintained among a system of particles as rest. Thus the one thing requiring to be admitted to account for all the effects of gravity is, that the universe is immersed in a gas the mean length of path of whose particles is great.

5. The other assumptions or postulates of Le Sage in connexion with his theory, viz. equal *density* in all parts of the streams of moving particles, equal *mean velocity* in all parts, follow no less as automatic consequences from the recent dynamical investigations connected with the kinetic theory of gases. Thus the conditions of Le Sage's theory become converted from a series of arbitrary assumptions or postulates, to a series of deductions following from the rigid principles of dynamics.

6. It forms a truly wonderful fact to consider, that a system

of bodies or particles left to themselves, with nothing to guide them but their own collisions (which might well be regarded as fulfilling all the essentials of a chaos), produces and maintains the most rigid system of order, such that the number of particles contained in unit volume of the system (taken anywhere) is equal, the mean velocity equal in all parts, the mean distance of the particles the same in all parts, and the particles are moving uniformly towards all directions in all parts. Such is the result produced by pure dynamics. In fact it may be said that leaving the bodies to themselves constitutes the most perfect system of control, for any interference whatever would disturb the regularity of the motions. This regularity of movement is not only naturally continued, but forcibly and automatically maintained against any disturbance,—such that if it were imagined that a system of bodies were purposely put in motion in the most chaotic manner possible, the motion would of itself in a short time become regular, or the whole would become a system of order and uniformity.

7. Clausius, as is known, has investigated a relation between the mean length of path of the particles of a gas and the diameter of the particles. From this investigation it follows that the mean length of path of the particle of a gas (*i. e.* the average distance which the particle moves before encountering another particle) increases in proportion as the square of the diameter of the particle diminishes. Thus by making the particle small enough, its mean length of path may be increased to any extent. No objection, evidently, can be made to this, for *à priori* one size of particle is just as likely as another. This minute size would render it possible for the particle to possess a high velocity without producing thereby disturbance or displacement among the molecules of ordinary matter; and this high velocity is necessary to accord with the observed facts of gravity. One velocity cannot be said *à priori* to be more likely than another. We must just be guided by the teaching of facts as to what the velocity is*.

* I have shown (Phil. Mag. June 1877) that a physical relation exists between the velocity of the particles of a medium constituted according to the kinetic theory and the velocity of propagation of a wave in the medium. Professor Maxwell has calculated (as given in postscript to the paper) the numerical value of this relation at $\frac{\sqrt{5}}{3}$. Thus it appears that if the velocity of propagation of a wave in any medium constituted according to the kinetic theory can be measured, then the velocity of the particles of the medium is given by dividing this velocity by $\frac{\sqrt{5}}{3}$. So, for example, the velocity of the molecules of air is given by dividing the

8. It is an interesting fact pointed out by Sir William Thomson (Phil. Mag. May 1873) that the distance through which gravity is effective would depend on the distance through which the gravific particles move before being intercepted by collision with each other (which is equivalent to the mean length of path of the particles). By assuming the distance of the stars to be a multiple of the mean length of path of the particles, it would therefore follow that the stars do not gravitate towards each other—this satisfying the condition for the stability of the universe. The assumption of all the bodies of the universe gravitating towards each other is evidently quite inconsistent with stability (as already pointed out by Professor Challis). All that we require to admit is that the effects of gravity hold through as great distances as we have observed them.

9. The distance through which gravity has been observed to act is well known to be but an infinitesimal fraction of the distance of the stars. It may therefore well be that the mean length of path of the particles of the medium producing gravity may be but an infinitesimal fraction of this distance. The column of the gravific medium intercepted between two stars would therefore *on the whole* be at rest, just as a column of gas is at rest between two bodies a visible distance apart (*i. e.* a distance which is a large multiple of the mean length of path of the particles of gas). Le Sage appears to have assumed that the mean length of path of the gravific particles swept through the universe; or he assumed that streams of matter came from the depths of space and passed entirely through the visible universe into space beyond*. This assump-

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velocity of sound in air by $\frac{\sqrt{5}}{3}$; so of other gases. Thus it appears that the velocity of a wave in any medium constituted according to the kinetic theory (such as the velocity of a wave of sound in air) is solely dependent on and proportional to the velocity of the particles of the medium: and this velocity of the wave is independent of the density or pressure of the medium, or of any thing else excepting the velocity of its particles.

* Le Sage assumed that a continual supply of matter from without was necessary for the maintenance of gravity in the visible universe, and that all but a very small fraction of this supply passed through ineffectively and was dissipated again in ultramundane space—a means apparently quite disproportionate to the end in view. We observe that under the principles of the kinetic theory no such supply is necessary, but that all the conditions requisite for gravity may be fulfilled by a medium pervading the visible universe, and which is at rest *as a whole*: or the gravific medium within the bounds of the visible universe may be compared to the air within a receptacle, which is, as a whole, at rest: and therefore there is no more waste of the matter producing gravity than if mundane matter did not exist. If we imagine, in analogy, a being extremely small

tion cannot but be regarded as fantastic, and, as we observe, is by no means necessary. The mean length of path of the particles, so far from being comparable to the dimensions of the visible universe, may be but an infinitesimal fraction of the distance of two of its primary components. All we require to admit is that the mean length of path of the particles of the medium is at least as great as the very limited range through which gravity has been observed to act; or, in order to explain all the observed facts, it is sufficient to admit that the universe is immersed in a gas (or medium constituted according to the kinetic theory) the mean length of path of whose particles is so adjusted as to cause the *minor* or secondary portions of the universe to gravitate towards each other*. Under the simple conception of a variation in the diameter of the particles of a medium, the mean length of path of the particles (and with it the range of gravity) is capable of adjustment with precision to any range. It would probably be difficult to imagine any more simple condition as a mechanical means to an end than this.

10. It is a necessary condition to Le Sage's theory (in order

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compared with the mean length of path of an air molecule, to be stationed in the centre of a receptacle containing air; then this minute observer would notice the air molecules passing continually in streams equally in all directions; and the observer, not being able to trace the beginning and end of the path of the molecules, would naturally imagine that the molecules were being supplied in streams from outside the receptacle, and, observing the continued regularity of the streams *equally* in all directions, would suppose that there must be some external mechanism supplying the streams of molecules equally and symmetrically. This is what would be supposed in the absence of the application of the principles of the kinetic theory to the case. On applying this theory, it is seen that the same result can take place without a supply of air: and that the adjustment of the streams of air molecules uniformly in all directions is automatic, or the inevitable result of dynamical principles.

* If two particles of a gas be conceived gradually to increase in size and mass, they will gradually lose their translatory motion and finally come practically to rest. If now the two enlarged particles be at a distance apart less than the mean length of path of the remaining particles of the gas, these two particles will gravitate towards each other under the dynamic action of the other particles of the gas which pass them in streams (the opposed faces of the two enlarged particles being sheltered from the streams). This condition of things probably occurs when a vapour condenses, when the gradually enlarging water vesicles which happen to be at a distance apart less than the mean length of path of the other molecules of the vapour will be driven together by the dynamic action of these molecules, thus accelerating condensation. Thus possibly effects of "gravity" may be imitated by gaseous matter on molecular scale, as is observed in the large scale of the universe. It may be observed that these are simply applications on a smaller scale of the dynamical principles of Le Sage's theory, and therefore the deductions hold if the premises are admitted to be possible.

that gravity may be sensibly proportional to mass) that the total volume of free space in a substance, in the form of interstices between the molecules or in their structure, must be great compared with the total volume of matter contained in the molecules themselves. Le Sage assumed the molecules of substances to have a sort of open structure in the form of cages with wide interstices. This condition of free interstices would be equally satisfied by assuming the molecules to be small relative to their mean distance, or on the condition of the vortex-ring atom theory, without any necessity for making the above somewhat fantastic assumption of cage-structure.

11. It is necessary to assume that the particles producing gravity are in very close proximity compared with molecules, otherwise the particles would be unable by their motion to produce a perfectly equable pressure upon the molecules of matter. It might be thought that, because the particles of the gravific medium are so close, and the molecules of ordinary matter relatively far apart, therefore the quantity of matter in the form of gravific particles enclosed in a given volume of space must be very great compared with the quantity of ordinary matter that that same volume of space would contain—or, in other words, that there must be a relatively enormous quantity of matter in the form of gravific particles. This by no means follows; for although the gravific particles may be very close, the relative quantity of matter in them may be very small, provided the particles themselves are small. Indeed by simply conceiving an extreme degree of subdivision, the particles pervading a given volume of space may by continued subdivision be conceived to be brought into as close proximity as we please; and though the space itself is large, the total quantity of matter thus used may be conceived as small as we please. No consequence how minute the size (or mass) of a particle may be, the effect produced by its motion remains as great, provided its velocity be adequately augmented. The minute size is the very condition adapted to a high velocity; and this minute size is at the same time the necessary condition for a long mean path. Thus we may observe that the mechanical conditions of the problem fit into each other. The matter of the gravific medium is in such a finely subdivided state, and its motion so rapid, that its presence necessarily eludes detection. The pressure (termed "gravity") due to the motion of the particles of the gravific medium is no more difficult of realization than the pressure due to the motion of the molecules of air. If the motion of the molecules of air be unrecognized by the senses, how much more must this be the fact with the minute gravific particles; indeed it is difficult

to see what mechanical objection can be urged against this realization of the problem, which is extremely simple.

12. The theory of "action at a distance" being rejected, which is necessary in order to explain the facts at all, the effects of gravity can in principle be referred to only two conceivable causes. The tendency of two molecules of matter to approach each other can be referred (1) to a motion possessed by the molecules themselves disturbing the equilibrium of pressure of the medium between them; (2) to a motion possessed by the medium itself (in the form of streams or currents) acting upon the molecules. The first of these two conditions appears to be inadmissible, from the fact that we cannot interfere with or modify gravity at will, whereas we can very readily interfere with or modify the motion of the molecules of matter (as by adding or subtracting heat, for example). It therefore would appear that gravity must be due to some motion that we cannot interfere with, *i. e.* to a motion in the external medium which we cannot handle or which is beyond our control. Only one conclusion appears therefore to be possible here; and therefore it would seem that the theory of Le Sage can scarcely be regarded as a mere hypothesis, but rather as an irresistible deduction which is forced upon us in the absence of any other conceivable inference. Certainly, if simplicity be a recommendation, the theory needs no recommendation on that ground.

London, July 1877.

XXVI. *The Finite Integrals of certain Partial Differential Equations which present themselves in Physical Investigations. By the* Rev. S. Earnshaw, *M.A.*

To the Editors of the Philosophical Magazine and Journal.

Gentlemen,

THE Astronomer Royal, in his treatise 'On Sound and Atmospheric Vibrations,' has drawn particular attention to equations of the following general form,

$$\frac{d^2u}{dt^2} = \frac{d^2u}{dx^2} + \frac{a}{x}\frac{du}{dx}, \quad \ldots\ldots \quad (1)$$

and has expressed an opinion that equations of this class cannot be approached by any one general method of attack. The equation has been solved by the Astronomer Royal himself in a finite form for the two cases $a=0$ and $a=2$; but in other cases he has had recourse to infinite series, which, it is observed,

is an unsatisfactory form of an integral when its convergence is not assured.

Now on looking at the above equation, we see that $mt+h$, $\pm mx$, and $u+\mathrm{C}$ may be respectively written for t, x, and u without in any way affecting it—h, m, C being what I have elsewhere called *germs*, i. e. quantities capable of being considered either arbitrary constants or arbitrary independent variables. Hence we know that the integration of equation (1) comes within the Germ-integral Theory ; and by this theory the following results have been obtained:—

I. If $a=2n+b$, n being an integer, and if w be the integral of equation (1) when b is written for a, we have the following important formula,

$$u+\mathrm{C}=\left(\frac{d}{x\,dx}\right)^{n} w. \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

II. Hence, when a is an *even* integer and $b=0$, we have the following integral of (1) for this case,

$$u+\mathrm{C}=\left(\frac{d}{x\,dx}\right)^{\frac{a}{2}} \mathrm{F}(x\pm t). \quad . \quad . \quad . \quad . \quad (3)$$

(It will be perceived that $\mathrm{F}(x\pm t)$ is used as a brief representative of the sum of two independent arbitrary functions, $\mathrm{F}(x+t)$ and $f(x-t)$.)

III. If a be an *odd* integer and $b=1$, the integral of (1) will in this case be

$$u+\mathrm{C}=\mathrm{A}\left(\frac{d}{x\,dx}\right)^{\frac{a-1}{2}} \log\left(\sqrt{\frac{t}{x}+1}\pm\sqrt{\frac{t}{x}-1}\right) \quad . \quad (4)$$

when t^2 is greater than x^2; but when t^2 is less than x^2, then the integral takes the following form,

$$u+\mathrm{C}=\left(\frac{d}{x\,dx}\right)^{\frac{a-1}{2}} \left\{\mathrm{A}\cos^{-1}\frac{t}{x}+\mathrm{B}\sin^{-1}\frac{t}{x}\right\}. \quad . \quad . \quad (5)$$

But as these are what in the germ-theory are denominated root-integrals, it will be necessary, in order to convert them into general integrals, to write in them $t+h$ for t, h being t's germ.

IV. When a is *not an integer*, we find

$$\frac{du}{dt}=\mathrm{A}(t^2-x^2)^{-\frac{a}{2}}+\mathrm{B}(t^2-x^2)^{\frac{a}{2}-1}x^{1-a}, \quad . \quad . \quad (6)$$

or

$$\frac{du}{dt}=\mathrm{A}(x^2-t^2)^{-\frac{a}{2}}+\mathrm{B}(x^2-t^2)^{\frac{a}{2}-1}x^{1-a}, \quad . \quad . \quad (7)$$

the former or the latter to be used according as t^2 is greater or less than x^2.

Of course, to obtain $u+C$ from these, we have still to integrate once with regard to t. Nevertheless $\frac{du}{dt}$ is an integral of the proposed equation ; but it is not the complete integral. We have also to notice that, when this integration has been effected, we must then write in the resulting integrals $t+h$ for t.

Thus integrals of equation (1) have been found in finite terms when a is any integer whatever ; but in the remaining case, when a is not an integer, we have only found the general value of $\frac{du}{dt}$, which, however, is itself an integral in finite terms.

I will now turn to another general class of differential equations which has hitherto resisted all efforts to find a general integral of it. If we write $x^{\frac{1}{1-a}}$ for x, and t for $(1-a)t$ in equation (1), the result will take the following general form,

$$\frac{d^2u}{dt^2}=x^{\frac{2a}{a-1}}\frac{d^2u}{dx^2}; \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

which will be at once recognized as an equation which has never been integrated in finite terms, except in a certain class of particular cases. Its integral may be deduced from the results contained in II. and IV. by making the forementioned substitutions for x and t in them.

There is yet one other differential equation which is mentioned by the Astronomer Royal as being of importance in a certain problem of sound, and has not been integrated in finite terms. It is of the following form,

$$\frac{d^2u}{dt^2}=\frac{d^2u}{dx^2}+4a\frac{du}{dx}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

By the method of germ-integration the root-integral of this equation is found to be

$$u+C=\left\{\frac{A}{(x+t)^{\frac{1}{2}}}+\frac{B}{(x-t)^{\frac{1}{2}}}\right\}\epsilon^{-a(\sqrt{x+t}\pm\sqrt{x-t})^2}; \quad (10)$$

and this root-integral will become the general integral of the equation (9) if we write $t+h$ for t, and $x+k$ for x in it, h and k being the germs of t and x respectively.

Sheffield, August 17, 1877.

XXVII. *Notes on the Theory of Sound.* By R. H. M. Bosanquet, *Fellow of St. John's College, Oxford.*

[Continued from p. 136.]

FROM the above principles the proportion of the issuing energy which reenters the tube can be immediately deduced. In the case of outward flow, one fourth of the issuing energy reenters the tube; in the case of inward flow, the whole. (The reentering quantity is measured in the first case by

$$\int_0^\infty \frac{d\mathrm{S}}{\mathrm{S}^2}\,\frac{\mathrm{S}_0^3}{\mathrm{S}^3};$$

in the second case by

$$\int_0^\infty \frac{d\mathrm{S}}{\mathrm{S}^2}.)$$

If the air is flowing outward half the time and inward half the time, the energy lost in a complete period will be half the whole; if the period be not divided symmetrically between the inward and outward flow, the case will be different. It is difficult to submit this to the test of experiment; but it may be done in simple cases by testing the resonance to tuning-forks differing in pitch from the proper note of the resonator or pipe considered.

The following approximate result of experiment is now enunciated, so far as I am aware, for the first time.

The character of the sympathetic vibration of all resonators which communicate with the outer air by simple openings is approximately the same when referred to Helmholtz's scale (Ellis's 'Helmholtz,' p. 213); *i. e.* the difference of pitch in the exciting tone which reduces the intensity to $\frac{1}{10}$ is the same; and the number of vibrations after which the energy of the vibration reduces to $\frac{1}{10}$ is the same. I had been under the impression, the origin of which I cannot now trace, that resonators which had apertures small compared with their length stood higher in the scale of retention than such as have large apertures. It is on experimental grounds that I have come to recognize the fallacy of this. The following is the simplest crucial experiment.

A bottle resonator with small aperture resounds to $e\flat''$. A brass tube about an inch in diameter, open at both ends, resounds to the same note. A c'' fork, a minor third below, is struck, and rapidly passed over the apertures of bottle and tube alternately. If the experiment is properly arranged, the sympathetic response is about equal in the two cases.

(It is necessary to take care and arrange the tube in the most advantageous position for hearing, which is with the two ends equidistant from the head. If the tube is held upright with one end near the face, no response will be heard from it at all.) If the openings are then partially covered, so as to bring both resonator and tube into tune with the fork, the maximum resonance is also about the same in both cases.

The response in the case of a minor third is faint but quite audible; it is not inconsistent with the supposition that it is in amount $\frac{1}{10}$ of the maximum response. Now, if the loss of energy is equal in amount to $\frac{1}{2}$ the whole store in each vibration, according to the preceding reasoning it would take a little over 3 vibrations to diminish the store to $\frac{1}{10}$ (for 3 vibrations would diminish it to $\frac{1}{8}$). This would correspond to the 7th step of Helmholtz's scale, which is as follows (*l. c.*):—

	Difference of pitch which reduces sympathetic vibration to $\frac{1}{10}$.	Number of vibrations after which intensity of tone (? energy of vibration) reduces to $\frac{1}{10}$.
7.	Minor third.	3·17

We may assign both our experimental and theoretical results to this case without substantial discordance, considering the small degree of accuracy of the estimations.

It only remains to give some account of the experimental determination of the position of the centre of phase. In Helmholtz's memoir in *Crelle*, lvii., Wertheim's results are stated as follows:—

Mean for pipes open at both ends = ·663 R, the determinations ranging from ·56 R to ·82 R.

Mean for pipes closed at one end = ·746 R, the determinations ranging from ·64 R to ·86 R.

I have to thank Lord Rayleigh for lists of the Wertheim determinations, with the numerical results reduced to the present form. These accord substantially with the above account, making the means ·665 R for open pipes and ·766 R for stopped pipes. The discordances of separate experiments are greater according to these lists than according to Helmholtz's account.

The open pipes considered are plain cylinders, not organ-pipes; and the datum to which the number refers is the correction to the length for *one* open end, the same quantity that I call the distance of the centre of phase of the reflected vibration from the end of the pipe.

The results of Zamminer, also quoted by Helmholtz, are rather wild. They appear to show a diminution of the correction *with* the wave-length, and vary from ·85 to ·5 R for

open pipes, and from 1·3 to ·38 R for stopped pipes. Helmholtz assumes in this memoir that his solution for the case of a flange (hemispherical divergence), which is $\frac{\pi}{4}(=\cdot 785)\,\mathrm{R}$, agrees sufficiently well with the experimental results.

Lord Rayleigh noticed that the effect of a flange could be determined experimentally, and has recently determined it at ·2 R. I have determined it at ·25 R. If we admit ·8 R as the value of the correction for hemispherical divergence (intermediate value between $\frac{\pi}{4}$ of Helmholtz and ·82 of Rayleigh), we have ·55 R as the value deduced from the hemispherical case supposed known. (I do not express a decided opinion as to the logical cogency of the old investigations; it appears to me to fail, if the considerations I have urged concerning the form of outward flow be admitted.)

I now come to my own determinations of the corrections for open ends. The question resolves itself entirely into one of Tonometry; and after the light recently thrown by Mr. Ellis's indefatigable comparisons on the errors of the standards in ordinary use, it is not astonishing if the tonometry of the old experimenters can now be improved on. The only experiments I shall cite here were made after some experience had been gained; they were all carried out by comparisons with forks which I copied myself from Appun's tonometer at South Kensington. I do not, however, cite them as final. The error of the transfer to the forks, and of any subsequent alteration (to which forks are known to be liable), though small, can still be avoided. If at some future time I am able to employ a tonometer under such circumstances that I can myself verify it and then use it directly, I am satisfied that the discordances still outstanding may be further reduced.

The comparison of notes was made in all cases by blowing short discontinuous jets of air across the open end of the pipe. The pipe is not actually made to speak; but as the disturbance subsides a faint sound, not clear, but of perfectly definite pitch, is emitted, which is due to the vibrations of the resonator as it dies away in its own pitch.

If I come at any future time to the discussion of the theory of the speech of organ-pipes, it will be seen that the existence of a steady vibration generally (not always) involves a departure from the natural pitch of the pipe. But it is known that the pitch in which a vibrating body left to itself dies away is, for all practical purposes, the same as the natural pitch (note of maximum resonance). A good way of satisfying one's self that the note thus obtained is in-

dependent of the steady note produced by any particular mode of excitation is this. Take a bottle resonator whose pitch is about a minor third above that of a fork. Hold the fork to the bottle, and cover the mouth partially with the finger till the pitch is reduced to that of the fork, which is easily tested by blowing lightly; then by alternately raising the finger and applying it to the hole, the pitch of the resonator may be alternated between that of the fork and its own a minor third higher. Now, if the fork be held steadily to the mouth and the finger moved in this manner, the note of the fork is distinctly heard to be followed by the proper note of the resonator for an instant, the excited vibrations dying away in the proper note of the resonator.

I cite two experiments only with tubes open at both ends. These had their pitch so arranged as to fall in regions where I had forks at intervals of four vibrations copied from Appun's tonometer. The interval between two such forks is to my ear a gross quantity; and the division of the interval by estimation is more feasible than with larger intervals. In some cases I tuned a fork to the note to be determined, and then counted the beats it made with the forks on each side of it. In others I availed myself of the variation of temperature of the room, noting at what temperatures the tubes coincided with any of the standard forks. The velocity of sound at 0° C. was taken at 1087 feet per second (Note 1). $\frac{\lambda}{D}$ is the ratio of the wave-length to the diameter of the tube (approximate). The value of the correction is the difference between the length deduced from the observed note and the true length for *one* open end.

$\frac{\lambda}{D}$.	R.	Length.	Correction.
6	1 in.	5 in.	·635 R
15	·97 in.	14·1 in.	·543 R.

I regard these two as probably the best determinations I have. Both tubes were prepared of perfect form with great care; and the exact knowledge of the pitch, with the presence of two open ends, enables me to say that I do not think it possible that either determination can be in error by more than half the difference between the two. Under these circumstances I state the following as an experimental law. *The correction for the open end of a tube increases and diminishes with the ratio of diameter to wave-length.* I need hardly say that this does not rest only on these two observations; but they illustrate it.

I now come to tubes stopped at one end. These experi-

ments were all made with the tube employed in the second of the above determinations, to which a flat movable plug was fitted. I had some difficulty in getting the plug to fit perfectly; and, whether from this or some other reason, these determinations do not agree so perfectly as those given above. The method was to shift the plug till the note agreed with one of the tonometer-forks:—

$\frac{\lambda}{D}$.	Description.	Correction.
13	Mean from determinations of four adjacent forks about c''	·626 R
15	Mean of three forks about a'	·554 R
17	g'	·595 R
25	$c'\sharp$	·503 R
26	c'	·43 R.

That there are some inequalities and discrepancies here is evident; but they are less than those of Wertheim, and distinctly follow the law above announced.

Less weight attaches to these observations than to the two with both ends open; it is not practicable to ascertain the effective dimensions of a very short pipe closed by a movable stopper with any thing like the accuracy with which this can be done for a cylinder open at both ends. These results, however, distinctly negative the position which follows from Wertheim's numbers, that the correction for stopped pipes is greater than that for open ones. They do not furnish material for any distinction between the two.

The present experiments are those which were made with all care; they confirm the general conclusions I had arrived at previously by a considerable number of experiments of a preliminary character. I have not at present attempted an extensive series of experiments, as I cannot expect final results until I verify a tonometer myself and then use it directly.

The $c'\sharp$ fork used in the last experiment but one has been verified repeatedly; and I consider it the best single fork I have. I am confident that the error of that determination does not amount to 1 vibration out of 276, which would correspond to about ·04 R.

I must further quote one of my older experiments on a longer tube open at both ends. It is a piece of gas-pipe 33·2 in. long and exactly 1 in. in diameter. It gives a very clear note. I copied its octave (at 55° F.) on a fork; I then took up the fork and determined it at the tonometer at South Kensington. It was exactly 396; this gives the correction for one end = ·436 R. Calculating the vibration-number from cor-

rection = ·6 R, we find 394, a difference of two vibrations. Unless this was due to an alteration of the fork in the meantime, I am confident that an error of this amount could not have taken place.

The general conclusion I draw is, that the value ·55 R for an open end is about the mean of the values I obtain under various circumstances, and may be used provisionally until improved observations enable us to go further.

The 5-in. iron tube of 2 in. diameter was also used for the determination of the effect of a flange. Two grooves were turned on the outside edges of the tube, and two wooden circular flanges about 7 in. in diameter fitted, with faces flush with the ends of the tube. The interval between the note with and without the flanges I estimated at about $1\frac{2}{3}$ mean semitone, or about 11 : 12 in ratio. The reduced length of the tube being just 6 in., the change introduced was equivalent to $\frac{1}{2}$ an inch—·5 R for two flanged ends, or ·25 R for each flanged end.

The knowledge of the correction for the open end of a pipe may be applied usefully to obtain an approximate standard pitch for practical purposes. If we form a cylinder of gas-pipe, and measure the length, diameter, and temperature, we obtain the vibration-number from the formula

$$n = 1087 \frac{1 + \cdot 001\, t}{2(l + \cdot 55\, \mathrm{D})};$$

where $32 + t$ is the temperature (Fahr.), l the length, and D the diameter. The note is obtained very clearly by blowing short discontinuous jets of air across the end. The pipe must be left to acquire the temperature of the room, and handled quickly with gloves, or, better, placed in a stand. A pipe 25 inches long and $\frac{1}{2}$ inch in diameter gives a medium modern c'. A wider pipe of the same length gives a somewhat lower c'. The note can easily be got correctly in this way within say two vibrations.

The c'' forks sold vary in pitch through about a semitone; modern forks being generally about 544, and most of those sold as 512 being from 520 to 530. Compared with such forks, notes obtained as above may be regarded as very accurate.

I have made one determination of the correction for a square pipe open at both ends. The pipe was made accurately of the same length as the iron pipe with the flanges; the side of the square was equal to the diameter of the iron pipe; and the edges were thinned off outside so as to leave nothing in the nature of a flange. The note is exactly that of the cylinder with flanges;

i. e. the correction is about ·88 R, where R is the half-side. It is quite possible to calculate the correction, according to the preceding principles, on the hypothesis of spherical divergence; but the result always comes out much less than the experimental value, even if a considerable allowance is made for the shortness of the pipe compared with the wave-length.

Errata in Note 6 (Phil. Mag. August).

Page 125, line 6 from foot of page, *for* vortical *read* vertical.
— — — 5 from foot of page, *for* vertical *read* vortical.
— 131, line 17, at the end of the line, *for* $\frac{dS}{S^3}$ *read* $\frac{dS}{S^2}$.

XXVIII. *On the Nature of what is commonly termed a "Vacuum."*

To the Editors of the Philosophical Magazine and Journal.

Queen's University, Dublin,
August 19, 1877.

GENTLEMEN,

THE readers of Mr. Preston's paper in this month's Number of the 'Philosophical Magazine,' "On the Nature of what is commonly termed a 'Vacuum,'" might perhaps suppose with him that the subject is one which had not been previously noticed, and conclude that we are as yet without an explanation of "Crookes's force," in which the vast multitude of the gaseous molecules that are present has been taken into account.

The subject is one which cannot, I should think, have been overlooked by any real student of the molecular theory of gases; and in particular your readers will find it thus treated in a paper that I presented ten years ago to the Royal Society (see Phil. Mag. [IV.] vol. xxxvi. p. 141):—"It is therefore probable that there are not fewer than something like a unit-eighteen of molecules" [*i. e.* 1,000000,000000,000000] "in each cubic millimetre of a gas at ordinary temperatures and pressures. Hence we may see how entirely remote from a state of emptiness that which usually passes under the name of a vacuum-chamber really is. If there be a unit-eighteen of molecules in every cubic millimetre of the air about us, there will remain a unit-fifteen" [*i. e.* a thousand millions of millions] "in every cubic millimetre of the best vacuums of our ordinary air-pumps. The molecules are still closely packed, within about an eighth-metre of one another; *i. e.* there are about sixty of them in a wave-length of orange light." And in two papers published in last year's 'Philosophical Magazine'

[V.] vol. i. pp. 177 & 305, I offered an explanation of the mechanical stresses within Crookes's radiometers based upon this very consideration: see in particular page 178, where the following words occur:—"I cannot refrain from observing here how entirely remote such a chamber" [viz. a Sprengel vacuum indicated by one tenth of a millimetre of mercury] "is from being empty. It follows from what we know of the number of molecules in gases at ordinary pressures, that the number remaining in this so-called vacuum will be somewhere about a unit-fourteen, *i. e.* one hundred millions of millions, in every cubic millimetre." After which I quote, in proof of this assertion, the determinations of the mean interval at which the molecules of gases are spaced, by Professor Loschmidt in 1865, by myself in 1867, and by Sir William Thomson in 1870.

It is plain, however, that Mr. Preston has done good service by recalling attention to the immense number of the molecules, and the consequent shortness of the excursions of each molecule between its successive encounters with other molecules; since the subject was new to himself, and had been overlooked by some of the writers upon Crookes's radiometer.

I am, Gentlemen,

Yours faithfully,

G. Johnstone Stoney.

XXIX. *Notices respecting New Books.*

The Whitworth Measuring Machine, including Descriptions of the Surface-plates, Gauges, and other Measuring Instruments made by Sir Joseph Whitworth, *Bart., C.E., F.R.S., D.C.L., LL.D., &c. By* T. M. Goodeve, *M.A., Barrister-at-Law, Lecturer on Applied Mechanics at the Royal School of Mines, and* C. P. B. Shelley, *Civil Engineer, Honorary Fellow of, and Professor of Manufacturing Art and Machinery in, King's College, London. With* 4 *plates and* 44 *woodcuts.* London: Longmans, Green, and Co. 1877. (Fcp. 4to, pp. 84.)

As an instance of the importance to mechanical engineers of very small differences of size, Sir J. Whitworth, in a paper read in 1857, took the case of "an internal gauge having a cylindrical aperture ·5770 inch diameter, and two external gauges, or solid cylinders, one being ·5769 inch and the other ·5770 inch diameter. The latter is 1-10000th of an inch larger than the former, and fits tightly in the internal gauge when both are clean, and dry; while the smaller ·5769-inch gauge is so loose in it as to appear not to fit at all." He remarked, that it was plain from this instance, "that the difference between these two cylinders is an appreciable and important quantity," and he added that "when a

good workman becomes familiar with such sizes as ·001 and ·0001 of an inch, he will not rest satisfied until he can work with corresponding accuracy" (pp. 73, 74). The instrument whereby the workman is enabled to become practically acquainted with these minute divisions, is the workshop measuring-machine; the primary object of which is the construction of accurate difference-gauges, *e. g.* of a series of solid cylinders whose diameters shall form an arithmetical progression having a common difference of 1-5000th of an inch. It consists essentially of two small planes accurately parallel to each other, and capable of being adjusted at any assigned distance by means of screws with accurately divided heads. The article to be measured (say a solid cylinder) is placed between these planes, and one of them is moved forward until the cylinder experiences in passing between them a slight resistance, the intensity of which can be judged of by the touch; the distance between the planes can then be determined by reading the screw-heads. As the planes touch the cylinder, their distance is its diameter. The machine resembles a small turning-lathe: it consists of a cast-iron bed and two head-stocks, one fixed, the other capable of being moved along the bed by a double-threaded screw of a half-inch pitch. By this screw the movable head-stock can be quickly placed in an approximately right position. The measuring-planes are the ends of cylindrical pieces exactly fitted into cylindrical holes in the head-stocks; they are caused to advance and recede by screws with 20 threads to the inch—the head of the screw in the movable head-stock being divided into 250, that in the fixed head-stock into 500 equal parts. There are therefore three graduated parts, viz. a scale of inches on the bed, a screw-head reading to 1-5000th of an inch in the movable head-stock (A), and a screw-head reading to 1-10000th of an inch in the fixed head-stock (B). Suppose it is required to produce a gauge 4·003 inches in diameter. The screw-head B is set and read; the movable head-stock is brought up to the four-inch graduation on the bed, and clamped; the screw-head A is then turned till a 4-inch standard gauge just passes freely between the planes, which are now four inches apart; the wheel B is then set back 30 divisions, making the planes 4·003 inches apart; and the piece of metal is gradually formed till it has perfect but free contact with the planes. When the true adjustment has been given to the machine, it is found that an increase or diminution of the distance between the planes corresponding to a quarter of a division of the large screw-head, and amounting therefore to 1-40000th of an inch, causes a distinctly perceptible diminution or increase in the resistance which the object encounters in passing between them, and consequently the error in the diameter of the gauge ought not to exceed the 40000th part of an inch.

When the object in view is to produce an exact copy of a standard of length, *e. g.* of a standard inch, a machine called "the millionth-measuring machine" is used. This is constructed on a similar plan to the workshop machine, above described; but now the head-stocks are both fixed, and the measuring-planes are wrought on the

ends of rectangular bars which slide in right-angled V-shaped grooves. The measuring-bar in the one head-stock is moved by a screw with a graduated head, one division of which corresponds to an advance of the bar through 1-5000th of an inch; the other is moved by a screw of 20 threads to an inch, on whose head are cut 200 teeth, which work with a second screw, the head of which is divided into 250 equal parts; so that one division of the head of this second screw corresponds to an advance of the measuring-plane through a distance of one millionth of an inch. It is not, however, safe to rely on the unaided sense of touch for judging of so minute a distance; the pressure of the measuring-plane against the end of the object under measurement is regulated by its sufficiency to support the weight of a small metal disk, interposed between the object and the plane; it is found that this disk (or gravity-piece) will fall between them when their distance has a certain amount, and will be supported when that distance is diminished by a millionth of an inch.

It is plain, from the above description, that the construction of these machines depends upon an extreme accuracy in the workmanship; the method would manifestly fail unless the measuring planes were truly plane and accurately at right angles to the axes of the sliding bars. To Sir Joseph Whitworth belongs the honour of devising the means of obtaining the needful extreme accuracy of workmanship, as well as the modes of applying it to the construction of these measuring-machines. If two pieces of metal are machine-planed, and one of them is smeared with a film of red ochre and oil, on placing it carefully on the other, the bearing-points become apparent, and can be reduced by scraping, until a contact can be attained which is sensibly at all points of the surface; this process of scraping, as distinguished from polishing, admits of being performed with extreme exactness. Now, if three pieces (A, B, and C) are taken, and the process of scraping performed on them till A coincides with B, B with C, and C with A, the surfaces of all three must be planes; and when the operation has been performed with all the exactness of which it is capable, they are said to be *true planes*. Strictly speaking, each of the pieces has an indefinitely great number of evenly distributed bearing-points, which lie on a surface differing from a true plane, by an amount insensible to any test that has hitherto been applied.

These "true planes" once formed, there is comparatively little difficulty in forming others; and numerous applications can be made of them, *e. g.* the formation of the sliding bars and V-shaped grooves in the measuring-machine. Take three nearly rectangular bars (a, b, c); two of the opposite faces of each can be scraped until they coincide accurately in all positions with one true plane on which they rest, and a second true plane placed on them. Each bar now has two parallel faces, and in all three the distances of these faces is the same. This being done, let a third face of each (viz. x of a, y of b, and z of c) be wrought till they stand the following test:—The bars resting on one of their parallel faces on a true plane, x can be brought into perfect contact with z and likewise with y; b is now turned over

so as to stand upon its parallel face, and in this position y can be brought into perfect contact with z. It is plain that when this is done, x is at right angles to the parallel faces of a, y to those of b, and z to those of c. There will now be little difficulty in working the fourth face of each bar. These bars can now be used for bringing into exact shape a rectangular V groove cut in a block of metal; and when this has been done the measuring-plane at the end of the bar can be dealt with. Thus, the bar is placed with one edge (k) in the groove, and examined by a true plane; it is then turned through 180° so that the edge opposite to k is now in the angle of the groove; both the face of the block and the end of the bar are now formed until the contact of both with a "true plane" is perfect in both positions. A similar process is then performed when the bar has its remaining edges successively in the groove. When perfect contact in all these positions has been attained, the end of the bar is at right angles to its axis.

It is obvious that these tests depend on simple geometrical facts, which would yield perfect results if they could be perfectly applied; they are in fact applied with a degree of accuracy that comes indefinitely near to perfection.

We have dwelt so long on the machines and the principles involved in the construction of their parts, that we have little room to speak of the rest of the volume. This is the less to be regretted, as a good deal of it is controversial: *e.g.* the object of Chapter 2 is apparently to prove that the Committee on standards carried out a method for the construction of primary standards inferior to Sir J. Whitworth's. We must not, however, conclude our notice without just mentioning that several other topics are introduced besides those adverted to above—such as the adaptation of the measuring-instrument to the bores of guns, as well as others of a more general character, as the value of uniformity of system in mechanical work. The book, which will be seen to be one of great interest, is written very clearly and accurately, as might be anticipated from the names of its authors. The illustrations seem to have been executed with great care, and are very good; and, in particular, the four engravings of the measuring-machine are exceedingly beautiful specimens of mechanical draughtsmanship.

XXX. *Proceedings of Learned Societies.*

ROYAL SOCIETY.

[Continued from p. 151.]

March 15, 1877.—Dr. J. Dalton Hooker, C.B., President, in the Chair.

THE following paper was read:—

"Description of the Process of verifying Thermometers at the Kew Observatory." By Francis Galton, F.R.S.

It may be of interest to describe the method recently adopted at the Kew Observatory of verifying thermometers by comparison at different temperatures with a standard instrument, since a large proportion of the various thermometrical determinations made by

English physicists are dependent for their accuracy upon that of the verifications at Kew. Many thousands of thermometers have already been verified by the apparatus about to be described.

Up to the year 1875 the apparatus for this purpose at the Kew Observatory was of the rudest character.

It was simply a glass jar 9½ inches wide and 18 inches deep, filled with hot water and standing on a turntable, in which a brass frame was placed.

The thermometers were attached to this framework, and the observer having well agitated the water with a plunger, read the instruments in succession through the glass as he turned the jar round before him, reading each thermometer as it passed. He first turned it round from right to left, and then back again from left to right. Each thermometer was thus read twice, and the mean of the pair of readings was taken. It is obvious that if the rate of cooling of the water be uniform, and if the thermometers are observed at precisely equal intervals, the mean of every pair of observations would be strictly referable to the temperature of the water at the same moment of time, namely to that which is half-way between the beginning and end of the entire set. It is needless to point out that these conditions can never be strictly fulfilled, although, notwithstanding the imperfection of the process and the coarseness of the apparatus, the observers acquired much certainty and skill in its manipulation. Still the time occupied was unnecessarily great, and the chance of error, owing to variations in the rate of cooling of the water, was larger than it need be. Partly owing to this latter reason, and partly to the fact that the number of thermometers sent to be tested has considerably increased (being now not less than 3000 annually), I thought it advisable to design and propose to my colleagues of the Kew Committee the construction of an instrument of a much more substantial and adequate character; and to this the Committee assented. I was subsequently indebted for many suggestions to Mr. De La Rue, and also to Mr. R. Munro, of 24 Clerkenwell Green, London, by whom it was finally made. It has now been at work for two years, and its performance is quite satisfactory; experience has in the mean time suggested a few emendations and simplifications, and I will therefore describe the instrument as at present in use.

The apparatus (see figs. 1 & 2) consists essentially of four parts:—

(1) A water-vessel.
(2) An agitator, worked by a handle on the outside.
(3) An external heating arrangement.
(4) A frame on which to hang the thermometers, turned by a handle on the outside.

(1) *The Water-vessel.*

This is a cylinder of stout copper, 2 ft. 2 in. high and 1 ft. in diameter. In its base there is a central aperture through which the concentric vertical axes are passed, which respectively carry the agitator and the thermometer frame; the top of the cylinder

is entirely open; a vertical slit, 1 ft. 10 in. long and $4\frac{1}{2}$ in. wide, is cut in the side of the cylinder and the slit is glazed with a stout sheet of plate-glass, the joints being made water- and steam-tight by means of india-rubber packing.

The cylinder is placed inside a wooden box, taller than itself, and 1 ft. 5 in. square at its base, the space between it and the sides of the box being filled with sawdust, whilst the exterior of the box is completely covered with kamptulicon, in order to retain the heat of the water in the enclosed vessel as much as possible. An aperture somewhat larger than that in the cylinder is cut in the side of the box in front of it, and is also glazed with plate-glass.

A lid, containing 3 inches of sawdust, covered with a sheet of kamptulicon, can be shut tightly down on the top of the cylinder and box, the escape of the vapour given off during heating being provided for by means of a steam-pipe.

Pipes lead from the top and bottom of the water-vessel to an exterior pipe ending in a funnel above and a cock below, so that water may be poured in or drawn off from the vessel as desired.

The whole is firmly fixed to a stout wooden stand about 2 ft. high.

(2) *The Agitator* (see fig. 2).

A stout and hollow brass axis, $2\frac{1}{4}$ in. in diameter, passes vertically up through the centre of the base of the water-vessel, carrying three sets of helical vanes, one above the other, arranged so that the upper and lower vanes form segments of right-handed screws, whilst the intermediate vanes are left-handed. The inclination of every vane is adjustable.

The lower end of the axis passes through a stuffing-box in the bottom of the cylinder, and is connected by gearing to a crank-handle projecting outside the apparatus. It can be turned easily by the hand of the observer, who thereby is able to agitate the water throughout the whole depth of the vessel.

(3) *The Heating-Apparatus* (see fig. 1).

This is a copper tube 0·6 in. in diameter, which, issuing from the back of the water-vessel near the bottom, is carried through the wooden casing of the instrument, and is then coiled into a vertical spiral of six turns, gradually diminishing in diameter. The end of the tube is afterwards brought back into the water-vessel.

A cluster of Bunsen burners being placed beneath the coil serves to heat it and to make the water circulate inside the cylinder, thus warming the whole of its contents.

Experiment shows that, with the small coil used, 10 gallons of cold water can be boiled in about six hours from the time of lighting the gas; in practice, however, when it is required to test thermometers near the boiling-point only (mountain thermometers, for example) the apparatus is filled with boiling water out of kettles put on an ordinary fire.

A cone of sheet-copper is usually placed round the coil as a jacket, in order to retain the heat from the gas-burners as much as

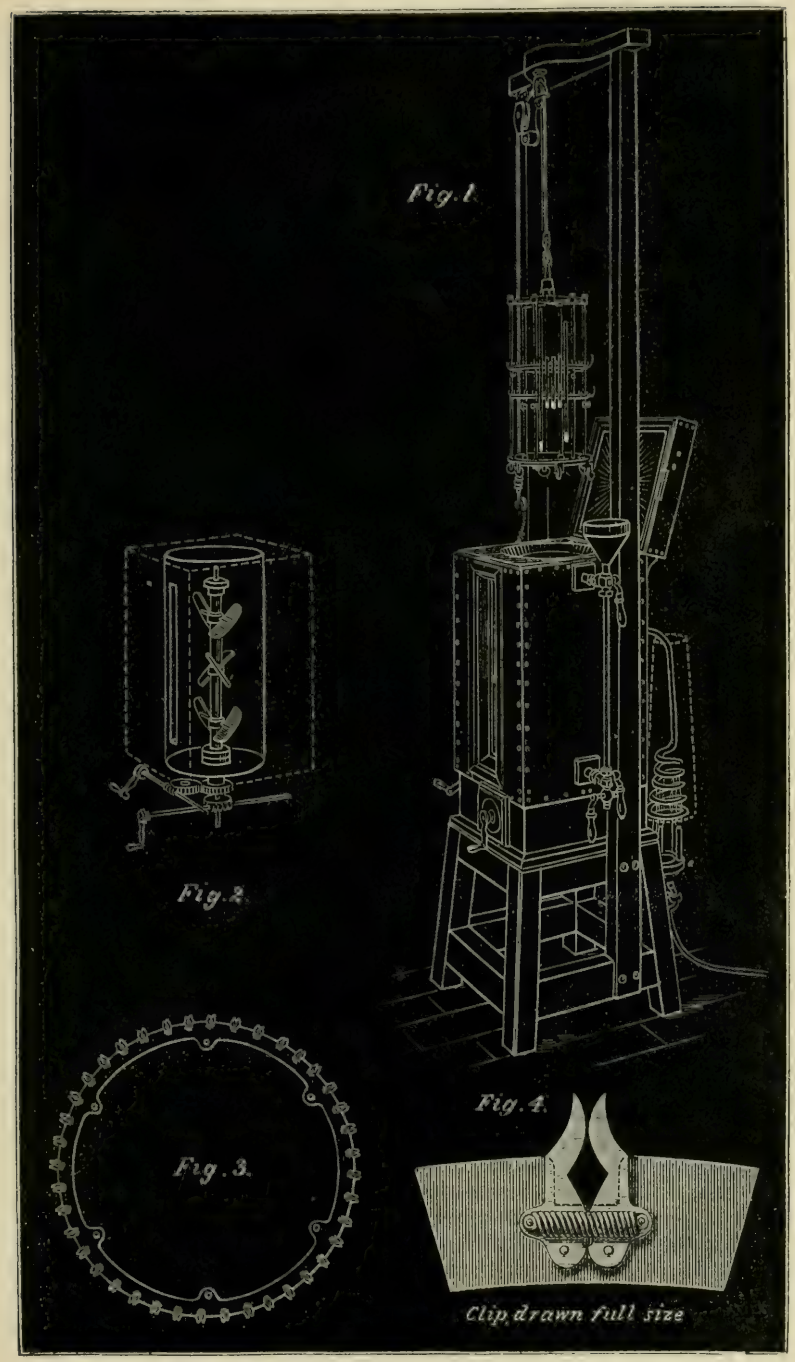
Fig. 1.
Fig. 2.
Fig. 3.
Fig. 4.
Clip drawn full size

possible; this is shown by dotted lines in the drawing. A cock at the lower end of the coil permits of the stoppage of the circulation of the water through the pipe.

(4) *The Thermometer Frame.*

The thermometers to be compared are hung side by side round the circumference of two brass rings, $10\frac{1}{4}$ in. in diameter, that are attached to the side rods of a cylindrical frame. The thermometers are held in their places against the ring by spring clips, one of which is shown full size in fig. 4, and one of the rings is shown in fig. 3; the latter slide up and down the brass rods that form the sides of the cylindrical framework, and are clamped at such a distance apart as may best suit the thermometer under examination.

Forty thermometers can be suspended at a time. The bottom of the frame is provided with six rollers—three placed radially, for the purpose of guiding it up and down the interior of the water-vessel; and three tangentially and projecting below the base, in order to support the frame whilst putting on or taking off the thermometers. This operation is performed when the frame is standing on the closed lid of the box, a circular brass ring being screwed to the lid to prevent the frame running off when being turned round by the operator.

The top of the frame consists of spokes radiating from a hollow socket that drops over the end of an upright steel rod, which, passing through the axis of the agitator, projects above it (see fig. 2). A plug is then screwed into the top of this rod and clamps the frame, which is supported by it; the frame, with the thermometers, can then be rotated in the water by turning this rod. This turning is effected from the outside through a wheel fixed to its projecting lower extremity, into which an endless screw, driven by a crank in front of the apparatus, is geared. The observer, facing the glazed slit, can bring the thermometers hung round the frame before him one by one as quickly as he likes.

For the convenience of moving the thermometer frame into and out of the water-vessel, a cord is carried over the apparatus round pulleys, as seen in fig. 1, so that the attendant can hook its end to the ring at the top of the frame, and twist or lower it with the greatest facility.

The general character of the process of comparison is to turn down the gas and to close circulation in the pipe by turning the stopcock; the water is then agitated, and is afterwards left at rest until the set is finished. The thermometer frame is turned once round forwards and once backwards in each process of comparison, each instrument being read off twice, the mean of the two being the result aimed at.

Mr. Whipple, the Superintendent of the Observatory, has made at my request a large number of experiments on the variations of temperature under different conditions, and on other matters relating to the working of the apparatus. It will be sufficient if I give a few summary tables of the results.

The mean variation of temperature during a double process of comparing each of twenty sets of thermometers, each set averaging nineteen instruments, and each instrument being read four times, was as follows :—

Temperature at which the comparison was made.	50°	70°	80°	90°	100°	110°
Mean variation during each set	+0·06	±0·07	±0·06	±0·07	±0·09	±0·15

The extreme variation of 0°·30 occurred in one case, and that of 0°·25 in three cases.

It takes about four minutes to read a complete set of ordinary thermometers.

The rate of heating by gas, and of cooling after the gas has been wholly turned off, is of course much affected by the temperature of the air of the room; it may be roughly taken as follows :—

When the water in the vessel is about ...	45°	100°	150°	200°
Rise of temperature in 5 minutes when the gas is turned fully on	2°·80	2°·26	1°·95	1°·45
Fall of temperature in 5 minutes when the gas is turned wholly off.....	.....	0°·25	0°·60	1°·00

The rate of cooling is much reduced when the process consists in first raising the water to the highest required temperature, and then cooling it by successive additions of cold water. The heat of the stuffing that surrounds the vessel being thus much higher than the water it contains, keeps it at an equable temperature.

The temperature of the water in the vessel, after agitating it and allowing it to settle, differs somewhat at different levels; this is due to the impossibility of securing perfect intermixture and to the variations of the temperature of the stuffing in respect to that of the water. The greatest differences observed between a thermometer whose bulb was immersed 2 inches below the level of the water and one that was immersed 19 inches was 0°·68.

March 22.—Dr. J. Dalton Hooker, C.B., President, in the Chair.

The following paper was read :—

"On Stratified Discharges.—IV. Stratified and Unstratified Forms of the Jar-Discharge." By William Spottiswoode, M.A., Treas. R.S.

It is well know that if a Leyden jar be discharged through a vacuum-tube, the discharge generally takes the form of an unbroken column of light, extending from the point of the positive terminal

to the hilt of the negative, *i. e.* to the extreme negative end of the tube, and that it shows no trace of either negative glow or intervening dark space. On the other hand I have found, by experiments with a large Leyden battery, that if a tube have one terminal connected with the negatively charged coating of the battery and the other held beyond striking-distance from the positively charged coating, the discharge in the tube will show a separation of the positive from the negative part by a dark intervening space. Under suitable circumstances of exhaustion it will also show striæ, in the same manner as when the discharge is effected directly with a Holtz machine, having the conductors either closed or open beyond striking-distance (see Roy. Soc. Proceedings, vol. xxiii. p. 460). Again, I have found, with the same battery, that if the tube be connected otherwise as before, and held at a distance less than at first, but a little greater than striking-distance, a stratified discharge much more brilliant and more like that produced by a coil will be exhibited. It should be remarked that the latter form of discharge appears to the unassisted eye, in the cases which I have examined, as an unbroken column of light, but with a negative glow and dark space. A revolving mirror, however, resolves the column into a regular array of striæ, having a rapid proper motion towards the positive terminal.

The transition from the first to the second of these forms, and from the second to the jar-discharge proper when the tube was brought within striking-distance, was, if not absolutely abrupt, at all events so rapid that this form of experiment gave no prospect of following one form into the other. With a view to examining the transition as closely as possible a Holtz machine was employed, and the jars having been taken off, a pair of mica plates partially covered with tinfoil was used in their stead. By sliding one plate over the other, so that more or less of the covered parts were brought face to face, a jar was formed the size of which could be varied at pleasure. An air-spark of adjustable length was also introduced into the circuit between the machine and the tube.

This arrangement was subsequently replaced by the following, which in some respects proved more convenient:—A battery of one or more jars was used in the place of the mica plates. The outside of this battery and one terminal of the tube were connected with the earth; and the inside and the other terminal were alternately connected with the positive conductor of the machine, so that the battery was alternately charged and discharged through the tube. The amount of charge was regulated partly by the distance through which the conductors of the machine were separated, and partly by the number of revolutions of the machine during which the charging took place. It was consequently independent of the absolute time of contact. It will be observed that this arrangement did not give the same opportunity of a continuous variation of jar surface as the first; but, on the other hand, the changes of phase in the phenomenon due to increments of charge were capable of indefinite diminution by shortening the distance between

the conductors of the machine and by increasing the number of the jars.

The first object proposed was to ascertain whether a jar could be charged with so small a quantity of electricity as of itself to give a stratified discharge in a tube; in other words, whether the resistance of the tube itself, if resistance it be, could by a suitable charge of jar be made to insure a stratified discharge. For this purpose a jar was charged with small sparks from the machine, and discharged after receiving charges of 1, 2, 3, &c. sparks in succession. The experiment proved successful with a coal-gas tube at a pressure of about 4 millims.: charges of three sparks gave bright flake-like stratifications; higher charges gave a discharge with a positive column, a negative glow, and a dark space, although the striæ were not always discernible. But when the charge exceeded 5 or 6 sparks, the positive column advanced so far as to obliterate the dark space, and ultimately made its way to the hilt of the terminal.

Similar experiments were made with both forms of instrumental arrangement, and with tubes containing different gases and at different pressures.

A number of tubes tried with various amounts of battery-charge, but with the same surface, showed that, as the charge was increased, the head of the positive column advanced towards the negative terminal, the dark space became narrower, and the glow contracted in dimensions; and when the head of the column drew very near to the negative terminal, the glow, instead of covering the whole surface of the terminal, formed a small drop at the point. On still further increasing the charge, the drop withdrew to the hilt of the terminal; and finally, when it had completely retreated into the hilt, the continuous or true jar-discharge took place.

With a view to testing experimentally how far the effects here described were due to quantity and how far to tension, the size of the jar was altered, all other circumstances remaining the same. It was then found not only, as before, that small charges gave stratified and large unstratified discharges, but also that the maximum charge compatible with stratification was greater with a large than with a small jar.

As a further experiment in this direction, a series of jars were arranged in cascade; and it was found that the greater the number of jars so arranged, the smaller the charge necessary to insure a true jar-discharge. A charge insufficient to destroy stratification with one jar was sufficient to destroy them when more than one was used in cascade. These results point to tension rather than to quantity as the determining cause of the character of the discharge.

In fact, having taken a number of jars of the same size, and having ascertained the maximum charge with which one jar could be charged without obliterating stratification, say, "the critical charge," I found that the critical charge for 2, 3, . . . jars arranged for quantity was 2, 3, . . . times that for a single jar; and, on the other hand, that the critical charge for 2, 3 . . . jars arranged

in series was 1 : 2, 1 : 3, . . . of that for a single jar. The illumination, however, was always greater with the larger charges, *i. e.* with the greater quantity of electricity discharged.

The experiments above described were made first with tubes in which the pressure was moderately high. They were afterwards repeated with lower pressures, and results of the same character as before were obtained. But, owing to the smaller amount of the critical charges, to the greater extension of the negative glow, and to the consequently increased delicacy of the phenomena, the same numerical precision was not attained. But there seems no reason to doubt that the discrepancies might be indefinitely diminished by instrumental refinements.

The duration of the stratified discharges observed throughout these experiments was exceedingly short, indistinguishable, in fact, from that of the true jar-discharge. When viewed in a revolving mirror, either with or without a slit, they showed no sign whatever of prolonged duration ; and we may thence conclude that, so far as our present instrumental arrangements extend, there is no inferior limit to the duration of discharge necessary for the production of striæ.

In connexion with this part of the subject another form of experiment was arranged. Beside the jars hitherto described another was used, having its inner surface connected with one terminal of the tube, and its outer with the other. When this disposition was made, the additional jar acted as a buffer, and produced a stratified discharge under circumstances which would without it have produced a true jar-discharge.

A comparison of the results here obtained with those detailed in Part II. of these researches shows that the phenomena produced by suitable disposition of the Leyden battery coincide with those produced by the induction-coil. With the coil it was found that (1) for a given electromotive force the column of striæ was shorter the larger the battery-surface or strength of current used ; (2) that the proper motion, when directed, as usual, towards the positive terminal, was more rapid the greater the electromotive force employed. With the Leyden battery (1) it was found that, in order to maintain the same length of column with an increased surface, the charge must be increased in a larger proportion than the surface ; and (2) it was noticed that the striæ, which when the tension was low were distinct and well separated, became more blurred as the tension rose, until they sometimes were blended into an apparently unbroken column of light. The presence, however, of the negative glow still showed that the true jar-discharge had not yet been reached.

GEOLOGICAL SOCIETY.

June 20th, 1877.—Prof. P. Martin Duncan, M.B., F.R.S., President, in the Chair.

[Continued from p. 153.]

5. " On Points of Similarity between Zeolitic and Siliceous Incrustations of recent formation by Thermal Springs and those observed

in Amygdaloid and other altered Volcanic Rocks." By Prof. A. Daubrée, F.M.G.S.

The author described the formation of zeolitic minerals by the infiltration of masonry by the waters of thermal springs at Plombières (Vosges), Luxeuil (Haute-Saône), Bourbonne (Haute-Marne), and near Oran in Algeria. In breaking through the wall of concrete, composed of fragments of stone and brick built by the Romans round the mouths of these springs, it has been found that the materials employed have undergone a great change by the long-continued action of the water. The cavities in the bricks are occupied by minerals, generally zeolitic, among the most abundant of which is chabasite, agreeing in all respects with the natural mineral. Phillipsite or lime harmotome also occurs, associated with the preceding, just as in the amygdaloidal trap of Iceland. In hollows of the calcareous cement small crystals of apophyllite occur, with pulverulent and minutely crystalline fluor spar, together with other minerals not identified, but resembling in character gismondine and scolezite. At Plombières hyalite occurs with the zeolites; and where the masonry is exposed to the full flow of the water there is a transparent gelatinous deposit which becomes white and opaque when dry, and is a hydrated silicate of lime analogous to okenite. Arragonite occurs generally in acicular crystals, but sometimes of the form called apotome by Haüy, found in iron-ore deposits and in some basalts. Calcite is frequently associated with the chabasite, as in Icelandic lavas. Halloysite is also met with at Plombières.

Besides the formation of geodes in the visible cavities, the whole substance of the bricks was found to be altered by contact with the water. This change rendered the originally friable brick very hard and compact; and microscopic examination showed that its minute pores were filled with colourless and transparent mineral substances. The author gave the following list of the minerals thus found—chabasite, Christianite(?), mesotype, hyalite(?), tridymite, chalcedony in radiate spherules, calcite, and some globular bodies of uncertain nature. The association of chalcedonic quartz with opal is interesting, as proving that silica may be deposited in the anhydrous form when the temperature of the surrounding medium does not exceed 70° C. Analysis showed that the amount of zeolitic substance added to the bricks is from 13 to 14 per cent. of the total weight.

This contemporary production of zeolites and other minerals identical with those found in amygdaloidal and many other altered volcanic rocks is regarded by the author as an experimental demonstration of the mode of formation of the latter, which are no doubt produced in a similar manner by the percolation of water through the substance of the rocks, conveying to, and depositing in, their cavities mineral substances dissolved during its passage. Zeolitic minerals, as he says, may therefore be considered a kind of "extract" of the rocks so subjected to continued lixiviation. And the process being effected independently of any peculiar conditions of heat and pressure, would seem to show that no such conditions are essential in the production of natural zeolites.

6. "On the Cretaceous Dentaliadæ." By J. S. Gardner, Esq., F.G.S.

7. "On a number of new Sections around the Estuary of the Dee which exhibit Phenomena having an important bearing on the Origin of Boulder-clay and the Sequence of Glacial Events." By D. Mackintosh, Esq., F.G.S.

In this paper the author minutely stated the results of repeated examinations of a number of new sections of drift-deposits, with a particular reference to the character of their bases and lines of junction between them. He described in detail the patterns exhibited by the grooved erratic stones of the shelly clays compared with irregularly scratched stones of the Lake-district. He then gave a particular account of the character of the two shelly clays, and assigned reasons for believing in their threefold origin—the local grit and broken shells accumulated by the sea, which at the time was fully charged with subglacial clay, and the erratic stones carried and dropped by floating coast-ice. He described phenomena proving that boulders must have *fallen* into the clay, and called attention to the varying directions of striæ on rock-surfaces (including some he had lately discovered), and their relations to the courses and cross-courses taken by erratic stones, some of which had travelled 200 miles. He then connected the special observations he had lately made with the results of many years' investigations extending around the basin of the Irish Sea, from Carlisle to Crewe, and from Crewe to Anglesey, and traced the horizontal and vertical extent of the three shelly drifts, and their relation to the mountain drifts of North Wales and the Lake-district. He stated many reasons for rejecting the idea that land-ice had distributed either of the two Boulder-clays he had described, but left it an open question whether the blue clay of North Wales, the Lake-district, the Yorkshire valleys, and parts of Lancashire, with its local stones, may not have been accumulated under land-ice. He concluded by stating that the paper was intended to be introductory to one on the correlation of the drifts of the north-west with those of the eastern and central parts of England.

8. "Discovery of Silurian Beds in Teesdale." By W. Gunn, Esq., F.G.S., and C. T. Clough, Esq., B.A., F.G.S., of H.M. Geological Survey.

The authors described the general physical characters of Teesdale, referring especially to the position of the Burstreeford Dyke, the whin, according to them, occupying a very different horizon at Forcegarth Hill and Cronkley Fell, so that the displacement indicated by it is probably 400 feet greater than has been supposed. This disturbance has brought up the beds which lie at the base of the Carboniferous series in the dale; and these are exposed in the banks of the Tees at the old Pencil Mill at Cronkley, where they were formerly worked up into slate pencils. They are soft shales, usually grey or greenish grey, sometimes yellowish green or purplish red. They are very indistinctly bedded, but show traces of what may be cleavage in some parts. From the character of the deposit, the character of the dykes of the district, and the fact that these

beds are not altered by them, the character of the veins traversing them, and an apparent unconformity between these beds and the undoubtedly Carboniferous beds overlying them, the authors come to the conclusion that this deposit is not of Carboniferous, but of Silurian age; and they indicate certain theoretical conclusions which follow from this determination.

9. "On the Superficial Geology of British Columbia." By George Mercer Dawson, Esq., F.G.S., Assoc. R.S.M., of the Geological Survey of Canada.

The author stated that the rock-striation and fluting on the south-eastern peninsula of Vancouver's Island shows that at one time a great glacier swept over it from N. to S., filling the Strait of Georgia, 50 miles broad in places, and having near Victoria a thickness of ice of over 600 feet. Traces of this glacier also occur on San-Juan Island, and on the coast of the mainland. The deposits immediately overlying the glaciated rocks, besides what may be *moraine profonde*, locally developed, are sandy clays and sands, arranged in water, and sometimes containing marine shells. The lower beds, at least, of these, were probably formed at the foot of the retreating glacier, the sea standing considerably higher than at present. The northern part of the Strait of Georgia and the fjords opening into it, and the fjords north of the Strait, show ice-action to a height of above 3000 feet. Terraces on the coast of the mainland are rare, and never at great elevations.

The interior plateau of British Columbia shows a system of glaciation from N. to S., traces of which have been observed above 3000 feet. Subsequent glaciation radiating from the mountains also occurs. The superficial deposits here are either unmodified or modified. The former, representing the boulder clay, occurs at nearly all heights up to over 5000 feet; the latter characterizes nearly all localities below 3000 feet, and is most extensively developed in the northern low country, where it forms a white silt or loess. The interior is marked with shore-lines and terraces up to 5270 feet. Moraines occur in great numbers, most of them marking stages in the retreat of glaciers towards the mountains, although some may have been formed in connexion with the N. and S. glaciation.

The sequence of events in the interior, according to the author, seems to have been as follows:—glaciation from N. to S., with deposit of boulder clay; formation of terraces by lowering of water-surfaces, accompanied or followed by a warm period; advance of glaciers from the mountains, and formation of lower terraces; and retreat of glaciers to their present limits. The glaciation of Vancouver's Island may have occurred during both cold periods or during the second only.

The author considers the assumption of the production of the N.-to-S. glaciation by an ice-cap to be attended with great difficulties, and seems to favour the notion of its being effected by the accumulation of ice on the country itself, and especially on the mountains to the N., filling the central plateau in going southward, and passing seaward through the gaps and fjords of the coast-range.

XXXI. *Intelligence and Miscellaneous Articles.*

ON THE ELECTRICAL AND CAPILLARY PROPERTIES OF MERCURY IN CONTACT WITH DIFFERENT AQUEOUS SOLUTIONS. BY M. LIPPMANN.

WHEN mercury is in contact with pure or acidulated water, one has only to add to the water a small quantity of certain substances in order to notably change two of the physical properties of the contact surface—the capillary constant or superficial tension, on the one hand, and, on the other, the electromotive force (that is to say, the difference of the electrical potentials) of the water and the mercury. The experiments which I have made on this question, in the laboratory of M. Jamin, and which I have the honour of submitting to the Academy, have conducted me to this very simple relation :—For each value of the electromotive force the capillary constant has a determinate value, and one only, *independent of the chemical composition* of the liquid. In other terms, *if for two different combinations the electromotive force is the same, the capillary constant is likewise the same.*

To verify this law, I at first employed the following very simple apparatus :—Two equal capillary tubes, T, T′, are placed vertically side by side, and communicate by their lower part with one and the same reservoir of mercury ; their upper extremities are furnished with two funnels, E, E′, to receive the liquids for experiment. If the same liquid has been put into both E and E′ (*e. g.* water to which has been added one sixth of its volume of sulphuric acid *), the capillary depression of the mercury is the same in both tubes, since all is symmetrical on both sides. In one of the tubes a little chlorhydric acid or a trace of bichromate of potash is added (the former of these substances augments, the latter diminishes the depression of the mercury) ; the meniscuses cease to be of the same height in both tubes. The reservoirs E and E′ are then put into electric communication with one another by means of a fine tube filled with acidulated water. The mercury meniscuses are immediately seen to begin to move towards the same horizontal plane, where they come to rest. The tube of communication has been traversed by an electric current of short duration, the effect of which has been to equalize the electromotive forces of the two meniscuses ; the equality of these forces has brought with it that of the capillary constants, which demonstrates the law enunciated. When the electric communication is suppressed the inequality of the electrical differences is reproduced, and at the same time the difference of level.

Another verification, of great nicety, has been obtained by means of a more perfect apparatus. A vertical tube, open at both ends, is tapered to a fine point at its lower extremity. It contains a column of mercury of about 40 centims. height, which is supported by the capillary pressure of the minute meniscus which is formed in the slender point. This point dips into a glass vessel V con-

* This acidulated has over pure water the advantage of well wetting the glass, which eliminates the variations of the angle of junction between the two.

taining dilute sulphuric acid, with which can be mixed substances suitable for causing the capillary constant of the meniscus to vary—such as chlorhydric acid, chromic acid, &c. The electrical difference of the meniscus can be maintained constant. For that purpose the mercury and the liquid under experiment are put in communication respectively with some mercury and acidulated water contained in a large vessel V′. It can then be ascertained that the changes in composition of the liquid V do not cause the position of the meniscus to vary; this can be verified by means of a microscope with a reticule. If the electrical communications described above be suppressed, the meniscus becomes, on the contrary, very sensitive to the changes of chemical composition of the liquid.

It is necessary to employ for these experiments substances which, in small quantities, act powerfully on the capillary constant; two aqueous solutions put into contact do not take sensibly the same electrical potential, unless they have nearly the same chemical composition. Between two very different liquids, such as chlorhydric and sulphuric acids, taken each pure and diluted, an electromotive force of contact is produced, which would complicate the experiment. As bodies active in small quantities we may mention (1) the hydro-acids and hyposulphite of soda, and (2) bichromate and permanganate of potash in the presence of acids. Chlorine, sulphurous acid, and carbonic acid, on the contrary, have but little action. Bromine and iodine act in the same direction as the hydrogen acids, and in the opposite direction to the oxidizing bodies, such as chromic acid.—*Comptes Rendus de l'Académie des Sciences*, July 16, 1877, tome lxxxv. pp. 142–144.

NOTE ON THE EFFECT OF CHROMATIC ABERRATION IN DISTANT VISION. BY B. THOMPSON LOWNE, F.R.C.S., ARRIS AND GALE LECTURER ON ANATOMY AND PHYSIOLOGY IN THE ROYAL COLLEGE OF SURGEONS, LECTURER ON PHYSIOLOGY IN THE MIDDLESEX HOSPITAL MEDICAL SCHOOL, OPHTHALMIC SURGEON TO THE GREAT NORTHERN HOSPITAL.

Mr. S. P. Thompson, in a communication on this subject published in the July Part of the 'Philosophical Magazine' speaks of chromatic aberration as if it were an advantage in distant vision. I fail to understand, however, how this can be the case. There can be no doubt that distant objects are seen with a predominance of the more refrangible blue and violet rays; an eye, therefore, which is emmetropic for such rays is hypermetropic for the less-refrangible red rays. Taking the dispersive power of the eye as equal to that of water, this hypermetropia amounts to two dioptrics. Such an eye would therefore have the red objects of the foreground more out of focus than if it were achromatic. An eye which is emmetropic for red would on the other hand have blue objects accurately focused, without any accommodation, if they were situated at a distance of half a metre from the eye. No doubt, if red and blue are situated on the same plane at the same distance from the eye, as the red requires the greatest effort of accommodation it will appear

nearer than the blue; but it can hardly be conceded that the eye has been modified that we should see the red pigments of a painting apparently nearer than the blue background. This cannot be the meaning of the author when he speaks of the disadvantage of an achromatic eye, and when he supposes that such an eye would in process of time lose its achromatism by variation and selection.

ON SOME REMARKABLE PHENOMENA IN GEISSLER TUBES. BY MM. REITLINGER AND VON URBANITZKI*.

One pole of a Ruhmkorff's induction-coil was connected with one of the electrodes of wide cylindrical (Wüllner's) discharge-tubes. The resulting alternating discharges in the tubes are divided by the action of an electromagnet into two current-threads, of which the one is attracted by an approached conductor, while the other (which corresponds to the inflowing of positive electricity into the tube), independently of the direction of the inducing current, is much more powerfully repelled. The effect of this preponderance of the repulsion is, that without a magnet the entire discharge appears to be repelled. The experiment is singularly successful in carbonic acid and carbonic oxide. The negative light, as already previously observed, is tolerably indifferent to the influencing bodies; but with pressures below 0·2 of a millim., on bringing the end of the glass tube into contact on two sides or on surrounding it with the cathode, the strata of the positive light move their own breadth towards the anode, so that the first of them touches the anode. In oxygen this process does not make its appearance.

While the glass generally exhibits a green fluorescence at the negative electrode, with the purest possible hydrogen it appears greenish yellow—with oxygen, carmine red; but in the latter, when a stratum of air is inserted in the circuit, it becomes again yellow-green and green.

A vacuum-tube which did not permit the current of the induction-coil to pass through it at 1 centim. striking-distance, did so between the poles of the magnet; accordingly, in correspondence with Hittorf's view, that which stopped the passage was situated at the cathode.

If a vertical cylindric tube be brought between the magnet-poles, and thereby the positive discharge pressed threadlike, in the equatorial plane, towards the glass, and the negative bent into the magnetic surface, then a third magnet-pole deflects the latter as if it were paramagnetically polar, but each of the strata as if they were diamagnetically polar. With alternating discharges in tubes connected at one end only with the induction-coil, there appears at the same wire electrode two differently coloured light-surfaces, perpendicular to each other—one axial and one equatorial, the latter only on one side of the wire. These phenomena cannot be deduced from the known laws of the reciprocal action between current-conductors and magnets.—*Beiblätter zu* Poggendorff's *Annalen*, 1877, No. 7, p. 416.

* *Wiener Anz.* 1877, pp. 100-104.

THE

LONDON, EDINBURGH, AND DUBLIN

PHILOSOPHICAL MAGAZINE

AND

JOURNAL OF SCIENCE.

[FIFTH SERIES.]

OCTOBER 1877.

XXXII. *On Picoline and its Derivatives.* *By* WILLIAM RAMSAY, *Ph.D., Tutorial Assistant of Chemistry in the Glasgow University* *.

IN my last memoir (Phil. Mag. Oct. 1876) it was remarked that the attempt to prepare pyridine, or bases of the same series, by passing hydrocyanic acid and acetylene through a red-hot tube was successful. I have repeated this experiment on a somewhat larger scale; the bases were purified by boiling them with nitro-hydrochloric acid; the salts were decomposed with sodium hydrate, and the liberated bases distilled over with water-vapour, neutralized with hydrochloric acid, and transformed into platinum chlorides. On ignition, the platinum was found to amount to 34·6 per cent., while pyridine platinichloride contains 35·4 per cent. of platinum. It therefore appears that a mixture of these bases, as well as condensation-products of acetylene, is produced by the mutual action of acetylene and hydrocyanic acid. The yield is extremely small; as before, not more than a few drops of the bases were obtained; but were all other proof wanting, their smell would afford sufficient proof of their formation.

Picoline cyanate.—The reaction which takes place between primary and secondary organic bases and cyanic acid made it appear of interest to ascertain the behaviour of a tertiary base under similar circumstances.

Pure picoline hydrochloride, prepared by adding excess of strong hydrochloric acid to picoline and distilling from a

* Communicated by the Author.

small retort, was mixed with excess of silver cyanate in the cold. The silver cyanate was converted into chloride with slight rise of temperature; the liquid acquired the smell of picoline, while at the same time a very pungent smell was observable. After the silver chloride had been removed by filtration, the filtrate, which had a strong smell of picoline, was placed to evaporate over sulphuric acid; after some weeks small indistinctly formed crystals separated. When these crystals were dissolved in water and warmed, picoline and a gas were given off; when heated alone, the salt fuses and evolves picoline in large quantity along with some ammonia, and crystals of cyamelide sublime. As was to be expected, picoline has no tendency to combine with, nor is it changed by, cyanic acid. The compound, when formed, is very unstable, and decomposes easily into its proximate constituents.

Compounds obtained by heating Picoline Platinichloride with Water.

10 grms. of picoline platinichloride were heated in a sealed tube with about 20 cub. centims. of water to 170° for some days. The salt dissolved completely in the water at the elevated temperature; but each morning, when the tube was cold, a large quantity had crystallized out. After three days very little separated in a distinctly crystalline form; but a very viscid oil sank to the bottom, while flocks of a sulphur-yellow colour deposited from the orange-coloured solution while cooling. The oil was boiled repeatedly with fresh portions of water; it separated into a soluble portion consisting of unaltered picoline platinichloride and a dirty yellowish-green powder insoluble in water. This powder was dried at 100°, and analyzed. The platinum was precipitated with sulphuretted hydrogen; and the chlorine was estimated in the filtrate.

0·2450 grm. of substance gave 0·1115 grm. of Pt and 0·3252 grm. of AgCl, equal to 45·51 per cent. of platinum and 32·81 per cent. of chlorine. These numbers correspond with the formula $C_6H_7N.PtCl_4$, which requires 45·60 per cent. of platinum and 32·87 per cent. of chlorine. The soluble portion of the oil, when evaporated, gave off abundant fumes of hydrochloric acid.

The sulphur-yellow powder was also dried and analyzed: 0·4455 grm. gave 0·1675 grm. of platinum = 37·59 per cent., and 0·4748 grm. of silver chloride = 26·35 per cent.

These numbers correspond with the formula $(C_6H_7N)_2PtCl_4$, which requires 27·02 per cent of chlorine and 37·58 per cent. of platinum. It is analogous to Anderson's chloride of platino-

pyridine obtained by boiling the platinum salt of pyridine with water.

The reactions showing the formation of these substances are :—

$(C_6H_7N.HCl)_2\,PtCl_4 = C_6H_7N.PtCl_4 + HCl + C_6H_7N.HCl$;

and

$(C_6H_7N.HCl)_2 . PtCl_4 = (C_6H_7N)_2\,PtCl_4 + 2HCl$.

I was unable to obtain a compound analogous to Anderson's double salt of pyridine platinichloride and chloride of platinopyridine. Supposing such a salt to exist, it would have the formula $(C_6H_7N)_2\,HCl . PtCl_4$. We should then have a series, the first three members of which differ from each other by a progressive loss of hydrochloric acid, while the last differs from the one immediately preceding by containing a molecule of picoline less; thus :—

Picoline platinichloride.....$(C_6H_7N)_2\,(HCl)_2\,PtCl_4$
{Double salt[1].....$(C_6H_7N)_2\,HCl . PtCl_4$}?
Platino-picoline chloride ...$(C_6H_7N)_2\,PtCl_4$
New compound.....$(C_6H_7N) . PtCl_4$.

That picoline is really evolved when the platino-picoline chloride is transformed into the new salt, was proved by heating some of the former to a high temperature with water. The dirty-yellow residue had a strong smell of picoline.

The compound $C_6H_7N . PtCl_4$ is soluble in hot caustic alkalies; and on cooling, brown flocks separate; no picoline is evolved even on continued boiling. $(C_6H_7N)_2\,PtCl_4$ also dissolves in alkalies; but on cooling, no deposit is formed, and on addition of hydrochloric acid it is again precipitated as before. It is very sparingly soluble in water; it, as well as the other compound, dissolves in hot picoline; but the new compound cannot be transformed into $(C_6H_7N)_2\,PtCl_4$ by this means; no picoline adds itself on; and when the picoline has evaporated, the new compound is left as a gummy mass, having the same composition as before.

It was also found impossible to transform $(C_6H_7N)_2\,PtCl_4$ or $C_6H_7N . PtCl_4$ into $(C_6H_7N)_2\,(HCl)_2\,PtCl_4$ by heating with strong hydrochloric acid; neither that acid nor nitric acid has any action whatever on these compounds.

The fact that they do not evolve picoline on treatment with alkalies affords a very strong presumption that they do not contain picoline as such; but in what manner the platinum is held in combination with the picoline is as yet inexplicable. The compound $C_6H_7N . PtCl_4$ has in so far an interest, that it

is not analogous to any known compound of platinum chloride with ammonia.

Oxidation of Picoline.—4 ounces of picoline were oxidized by Professor Dewar's process (Trans. Roy. Soc. Edinb. 1872, pp. 189–196) with potassium permanganate. After the reduced manganese had been removed by filtration and the unoxidized picoline recovered by distillation, the liquid was neutralized, boiled, and precipitated while boiling with excess of silver nitrate. The extremely bulky curdy precipitate was filtered through cloth, squeezed, and washed repeatedly with boiling water. It was then again stirred up with water till thoroughly disintegrated, and decomposed with sulphuretted hydrogen, or with hydrochloric acid. After the silver sulphide or chloride had been filtered off, the liquid was concentrated to a comparatively small bulk; on cooling, long white crystals of dicarbopyridenic acid, $C_7H_5NO_4$, filled the whole vessel. After these crystals were removed, the mother-liquor gave a second, but much smaller, crop on further evaporation; it was also collected, and the filtrate was set apart for further investigation.

The filtrate from the precipitate with silver nitrate contained but a very small amount of organic substance. I succeeded in isolating a small amount of oxalic acid from it, by precipitation with lead acetate. No organic acids, however, crystallized out when it was evaporated to a small bulk and mixed with sulphuric acid.

When dicarbopyridenic acid deposits from an impure solution, it crystallizes in hair-like needles of great length, which are anhydrous. This form, dissolved in hot water and recrystallized, deposits in plates resembling naphthaline, as remarked by Mr. Dewar. But these are not the only forms in which it crystalizes. If the long hair-like crystals be allowed to remain in water for some weeks, their shape changes to that of blunt prisms, apparently formed of a number of these plates agglomerated together. These latter crystals contain one molecule of water, as proved by the following estimation :—

0·3088 grm., after being heated to 100° for some hours, lost 0·0293 grm., = 9·49 per cent. $C_7H_5NO_4 . H_2O$ contains 9·83 per cent. of water.

None of the crystalline forms of this acid were sufficiently well defined to allow of the determination of their crystallographic constants. The acid has a remarkably sweet taste, but no smell. Its melting-point, when anhydrous, was found, by repeated determinations, to be 237°·5. On crys-

tallization from aqueous alcohol, in which it is more soluble than in water, the acid deposits in prisms, and from ether in hairs.

The acid has no basic properties; a portion evaporated to dryness with hydrochloric acid gained no weight, showing that no chloride was formed. Mr. Dewar's formula for dicarbopyridenic acid was confirmed by analysis of the acid, as well as of a number of its salts.

0·3872 grm. gave 0·7109 grm. CO_2, and 0·1119 grm. H_2O. = 51·26 per cent. C, and 3·28 per cent. H. Theory for $C_7H_5NO_4$—carbon 50·30 per cent., hydrogen 3·00 per cent.

When heated to its melting-point, the acid decomposes into carbonic anhydride and pyridine; hence its formula is written $C_5H_3N(COOH)_2$.

Salts of Dicarbopyridenic Acid.

The *neutral potassium salt*, $C_5H_3N(COOK)_2$, was prepared by neutralizing the acid with potassium carbonate and evaporating. It is extremely soluble in water. When its solution is evaporated over sulphuric acid, it deposits in needles containing 1½ molecule of water.

After drying at 100°, 0·4030 grm. lost 0·0416 grm., = 10·32 per cent. The loss, corresponding to $2H_2O$, should amount to 12·90 per cent., and to 1½ molecule of water to 10·00 per cent.

The *acid potassium salt*, $C_5H_3N\begin{cases}COOH\\COOK\end{cases}$, is prepared by adding a molecule of the acid to a molecule of the neutral salt. It is much more sparingly soluble in water, and crystallizes in small globular masses consisting of tufts of needles radiating from a common centre.

The *sodium salt* forms very soluble white crystals.

Ammonium Salt.—A solution of the acid in alcohol gives, on addition of ammonia, a precipitate consisting of small plates. These plates, viewed by polarized light under a microscope, exhibit phenomena similar to those with selenite. Interference is produced, the result of which is that the plates exhibit different colours, the colour depending on the thickness. But each single plate of the ammonium salt exhibits a regular gradation of colour without any break of continuity. Does this mean that the opposite sides of the plate are not parallel to each other?

Calcium Salts.—The neutral salt, $C_5H_3N(CO_2)_2Ca$, is soluble in a large quantity of water. During evaporation of its solution to a small bulk, the salt deposits very small

needle-shaped crystals. It is very slightly more soluble in hot than in cold water, and cannot be obtained in large crystals by cooling a hot solution, nor by allowing a solution to evaporate over sulphuric acid. It contains no water of crystallization.

0·2510 grm., dried at 100°, gave 0·1198 grm. $CaCO_3$,= 0·0479 grm. Ca,=18·63 per cent. of Ca. $C_5H_3N(COO)_2Ca$ requires 19·51 per cent.

The neutral salt does not dissolve in excess of the acid. It may be prepared either by boiling a very dilute solution of the acid with calcium carbonate, or by mixing very concentrated solutions of calcium chloride and the acid ammonium salt of dicarbopyridenic acid.

Barium Salts.—The neutral salt, $C_5H_3N(COO)_2Ba + H_2O$ (Ba found, 42·81 per cent.; calculated, 42·54: H_2O found 6·24 per cent.; calculated, 5·62), is formed by dissolving barium carbonate in a very dilute solution of the acid. In its properties it closely resembles the calcium salt. It crystallizes in microscopic plates. The acid salt is a very insoluble white powder.

The *neutral zinc salt* crystallizes from a dilute solution allowed to stand over sulphuric acid in well-defined octahedra.

The *lead salt* is sparingly soluble in water, and crystallizes out, when a hot solution of the ammonium salt and lead acetate are mixed, in short small prisms, which are without action on polarized light.

There are two *copper salts*, one of which forms light-blue needles with a satin-like lustre; the other crystallizes in dark blue prisms. The former is sparingly, and the latter easily, soluble in water.

The *cadmium salt*, prepared by adding cadmium chloride to the acid, is a white, very sparingly soluble precipitate; it contains no water of crystallization.

With *ferrous salts*, dicarbopyridenic acid, or any one of its soluble salts, gives a red colour, closely resembling that of ferric sulphocyanide. This forms an excellent test for the presence of the acid. *Ferric salts* produce no change of colour nor precipitate.

The *manganese salt*, $C_5H_3N(COO)_2Mn.H_2O$, was prepared by adding manganese carbonate to the acid. The carbonate dissolved at first; but a white salt of the above formula came down after some time. It is sparingly soluble in water.

0·2212 grm. lost at 110° 0·0164 grm.,=7·41 per cent. Theory demands 7·56 per cent. 0·2212 grm. gave 0·07090 grm. Mn_3O_4,=23·05 per cent. Mn. Theory requires 23·10 per cent.

Two *silver salts* were formed—the acid salt by precipitating the acid in presence of nitric acid with an insufficient quantity of silver nitrate, and the neutral salt by adding excess of silver nitrate to the acid or its potassium salt. They are both white gelatinous precipitates when precipitated from cold solutions; but from boiling solutions they come down in a curdy state. In the latter form they are easily filtered through cloth. They are enormously bulky, and almost, although not quite, insoluble in water. They are not quickly discoloured by light.

Neutral salt $C_5H_3N\begin{cases}COOAg\\COOAg\end{cases}$.

I. 0·3057 grm. gave 0·1720 grm. Ag, = 56·26 per cent.
II. 0·5209 grm. gave 0·2943 grm. Ag, = 56·49 per cent.

Theory requires 56·69 per cent.

Acid salt.—$C_5H_3N\begin{cases}COOH\\COOAg\end{cases}$.

I. 0·3355 grm. gave 0·1313 grm. Ag, = 39·1 per cent.
II. 0·2005 grm. gave 0·0777 grm. Ag, = 38·75 per cent.

Theory requires 39·41 per cent.

When heated, these salts behave like mercury sulphocyanide, leaving a very light porous mass of metallic silver.

All the salts of dicarbopyridenic acid, when heated, give off a basic smell resembling that of pyridine, while a small carbonaceous residue is left.

Dicarbopyridenic Chloride.—Five grms. of acid were mixed in a small retort with 13·5 grms. of phosphoric chloride. The reaction soon commenced, hydrochloric acid and phosphoryl chloride being abundantly evolved for about an hour. The mixture was then heated, and all the volatile contents of the retort distilled over; a small quantity of charcoal was left. The last portions of the distillate solidified. The whole of the distillate was redistilled; phosphoryl chloride came over below 110°; and after it had ceased to distil over, the mercury rose very rapidly to 284°, at which temperature the chloride distilled. It was washed with cold water once or twice, and dried, first between folds of blotting-paper, and then over sulphuric acid.

The chloride is insoluble in water, soluble in alcohol, with decomposition, and very sparingly soluble in ether. When melted, and allowed to cool, it solidifies in long needles, which shoot out from the sides of the vessel into the still liquid portion. Its melting point is 60·5–61°. It is a compara-

tively stable body, as water when cold has but slight action on it.

Amide.—From the chloride, the amide was prepared by passing anhydrous ammonia over it while hot. The amide is insoluble in water; it dissolves in a large quantity of hot alcohol; when this solution was evaporated over sulphuric acid, it came down as a white, apparently amorphous powder. It is also insoluble in ether, and possesses neither taste nor smell. It melts at 295·5–297° (uncorr.). When warmed, a sublimate of long needles was obtained, the melting-point of which was above the boiling-point of mercury. Whether this body was an amide or not I was unable to ascertain, as I had not a sufficient quantity at my disposal.

Methyl Ether.—The methyl ether was prepared in two ways:—first, by boiling the silver salt of the acid with methyl iodide in presence of alcohol; and, second, by ochobating the chloride with methyl alcohol. In both cases the same body was obtained.

When prepared by the first method, 12·5 grms. of the silver salt were boiled with 200 cubic centimetres of alcohol and 11 cubic centimetres of methyl iodide for some days. The liquid was concentrated to a small bulk; and small white crystals were deposited, which were redissolved in alcohol and recrystallized.

It was also prepared from the chloride by placing some in a dry flask, and adding to it anhydrous methyl alcohol. Heat was evolved, and the alcohol began to boil. When the action had moderated, the mixture was cohobated for some days, to ensure the complete conversion of the chloride into the ether. Most of the alcohol was then removed by distillation; and the ether crystallized out when its solvent had become cold. In both cases the substance obtained consisted of well formed modified rhombohedral crystals (?). The methyl ether melts at 117°·5; it is easily soluble in water, alcohol, and ether. It has a faint smell of mice. It was analyzed with the following results:—

0·4070 grm. gave 0·1640 grm. of H_2O, and 0·795 grm. of CO_2; H=3·98 per cent., and C=53·26. Theory demands 4·61 per cent. of hydrogen and 53·38 per cent. of carbon for $C_5H_3N(COO \cdot CH_3)_2$.

Aldehyde.—Two grains of the lime-salt were mixed with 3 grains of calcium formate, and distilled from a bulb made of combustion-tubing. The reaction began at a red heat. The distillate consisted partly of a yellow oil and partly of white crystals, which solidified in the tube of the condenser.

The crystals were easily volatile, both alone and with water-vapour,—and when boiled with potassium permanganate gave, after removal of the manganese, a white precipitate with silver nitrate, having all the properties of silver dicarbopyridenate.

The oil was redistilled with water-vapour; and the basic portion was transformed into a platinum salt. The portion of the double salt insoluble in water consisted of ammonium platinichloride, and the soluble portion of a mixture of pyridine and ammonium platinichloride, as was proved by the amount of platinum it contained. The percentage of platinum found was 37·03; 34·60 is the amount contained in pyridine platinichloride.

I had intended to reduce the aldehyde to the alcohol; but the yield of the former was so small that it would have been useless to attempt it. By far the greater portion of the calcium salt decomposed, with formation of pyridine and ammonia. Had it been possible to obtain the alcohol in sufficient quantity, it might have been reduced to the base with which it is related, having the formula of lutidine. A transformation such as this would have gone far to establish the relation of one member of the pyridine series to the others.

One method, however, remained. The acid when distilled with soda-lime yields pyridine, thus:

$$C_5H_3N(COOH)_2 + 4NaHO = C_5H_5N + 2Na_2CO_3 + 2H_2O.$$

Under similar circumstances, the methyl ether might give lutidine, provided lutidine be dimethyl-pyridine; or a base isomeric with lutidine, were that supposition false.

To decide this question, methyl-dicarbopyridenate was distilled with soda-lime at a heat approaching to redness. This operation was conducted twice—first with about 2 grams of the ether, and the second time with rather more than 5 grams. Hydrogen was evolved with great regularity during the whole distillation, no gaseous hydrocarbon being formed, as was proved by analysis. On explosion with oxygen, none of the residual gas was absorbable by potash: it consisted of pure oxygen. The distillate had a very strong basic smell. It was redistilled with dilute caustic soda, and divided into two portions. Both of these were neutralized with hydrochloric acid, and evaporated to dryness: one of them was mixed with nitric acid, and again evaporated to dryness; the nitric acid was then expelled by repeated evaporation with hydrochloric acid. Platinum tetrachloride was then added, and the precipitate fractionated. The first portions consisted of

pure ammonium platinichloride, the last of pyridine platinichloride. In no case did the amount of platinum found indicate that the base possessed a higher molecular weight than that of pyridine. Similar results were obtained with the portions which had not been boiled with nitric acid. It is therefore certain that no bases are found, the molecular weight of which is greater than that of pyridine, and probable that pyridine is the only base produced with exception of ammonia. This affords a strong presumption that lutidine is not dimethylpyridine; for, were it produced, it is certainly stable enough to resist decomposition by soda-lime.

Mr. Dewar mentions in his memoir that he obtained a mixture of dicarbopyridenic acid with another acid of much higher molecular weight, less soluble in water than the above-named acid. Of such an acid I could find no trace; but the mother liquor of dicarbopyridenic acid, by repeated fractional crystallization from alcohol, deposited very well-formed rhombic crystals, of which I had about a gram at my disposal. This acid gave off a smell of pyridine when rapidly heated, and when gently warmed sublimed, apparently without alteration. Its melting- and decomposing-point was 216°·5–217° (uncorr.), while that of dicarbopyridenic acid, taken at the same time with the same thermometer, was 237°·5. With ferrous salts, dicarbopyridenic acid gives a deep-red coloration, while the new acid gives a yellow colour like that of ferric chloride. The basicity of the new acid, determined by titration with standard potash, was found to be 152: the potassium salt contained 33·85 per cent. of potash; the molecular weight of dicarbopyrdenic acid is 167; and its potassium salt contains 32·11 per cent. of potassium. The new acid is extremely soluble in cold water and in alcohol, whereas dicarbopyridenic acid is sparingly soluble in cold water. The acid, as well as its lead-salt, which is moderately soluble in water, and crystallizes in radiated crystals, was analyzed with the following results:—

0·4016 grm. of the acid lost, at 110°, 0·0723 grm. This loss consists partly of water and partly of volatilized acid, as I afterwards ascertained. 0·3293 grm. gave 0·5630 grm. CO_2, and 0·1154 grm. H_2O, = 46·59 per cent. of carbon and 3·83 per cent. of hydrogen.

The carbon and hydrogen in the lead-salt were also determined; the lead was unfortunately lost.

0·4122 grm. of the dry salt gave, on combustion with copper oxide, 0·3170 grm. of CO_2, and 0·0565 grm. of H, = 20·97 per cent. of carbon and 1·54 per cent of hydrogen.

Assuming the acid to be dibasic, it must contain four atoms of oxygen; and as it gave off a smell resembling pyridine when heated, it contains nitrogen, probably one atom. The basicity has been determined. Calculating the carbon and hydrogen contained in the lead-salts, from these data, to their percentage in the acid, the following are the results :—

	per cent.		per cent.
Acid . .	46·59	of carbon, and	3·83 of hydrogen.
Lead-salt calculated to acid.	46·83	of carbon, and	4·66 of hydrogen.

The formula agreeing most closely with the above results is $C_6 H_7 NO_6$, which requires 45·85 per cent. of carbon and 4·20 per cent. of hydrogen. Its potassium-salt would contain 33·53 per cent. of potash; the number found by titration was 33·85 per cent. I am far from assured that the above formula expresses the true composition of the new acid, and should willingly have investigated it more thoroughly, had not the great difficulty of separating it, and the small quantity in which it is obtainable, rendered it improbable that I should ever have procured enough for complete investigation. That it is distinct from dicarbopyridenic acid is sufficiently proved by its properties.

The silver-salt of the new acid is a jelly soluble in water with difficulty, and turns purple on exposure to light. Its ammonium-salt volatilizes with water-vapour: hence an attempt to determine its molecular weight by evaporation with ammonia was unsuccessful. The ammonium-salt gives no precipitate with salts of copper, zinc, dyad mercury, nickel, or tin. With salts of silver it gives a gelatinous precipitate, and with ferrous salts, as already remarked, a deep yellow colour.

Oxidation of Lutidine.—Dr. Wright supposed that dicarbopyridenic acid might possibly be produced by oxidation of lutidine present in the picoline used; but Professor Dewar's base, as well as that oxidized by myself, was practically free from lutidine. Mr. Dewar compares the oxidation of picoline to that of benzol; the resulting bodies in both cases contain more atoms of carbon than the substances from which they are derived. Toluol when oxidized is much more easily converted into benzoic acid than benzol is; but the oxidation products of lutidine contain no acid precipitate with silver nitrate of so low a molecular weight as dicarbopyridenic acid. When lutidine was oxidized in the same manner as picoline,

the reaction took place more quickly. The filtrate from the manganese hydrate was treated with silver nitrate, and the insoluble silver salts decomposed with sulphuretted hydrogen. The mixture of acids obtained dissolved in water with difficulty, and on cooling crystallized out in crusts. The acid was again dissolved in hot alcohol, in which it is sparingly soluble, and crystallized. It deposited in microscopic needles. Some of it was transformed into the silver salt, and ignited.

0·2913 grm. gave 0·6335 grm. of metallic silver = 45·82 per cent.

The molecular weight of the acid, if dibasic, is thus 257. No dicarbopyridenic acid could be discovered among the products of oxidation after crystallization. From a scarcity of material it was impossible to obtain enough of the acid giving the salt, the analysis of which is given above, for complete investigation. By the kindness of Professor Ferguson, to whom I have to express my deep indebtedness for kindly supplying to me the material for this research, I have now a larger quantity of lutidine at my disposal, and intend to examine its oxidation products more carefully. It is already certain that lutidine is not convertible into dicarbopyridenic acid by oxidation (that is, by transformation of two methyl into two carboxyl groups); and this circumstance, combined with the fact that it is not produced by the reaction

$$C_5H_3N(COOCH_3)_2 = 2CO_2 + C_5H_3N(CH_3)_2,$$

affords strong presumption that the members of this series do not differ from each other by containing a group of methyl more or less.

Dipicoline.—Nearly five years ago Professor Thomas Anderson left bottles containing pyridine and picoline, in which a considerable quantity of sodium had been placed. I opened the bottle containing picoline and sodium in the month of March of the current year. The contents of the bottle formed a yellow opaque mass, of the consistency of sirup, at the bottom of the bottle. The substance enclosed much free sodium, and had a black colour. It was spread out and exposed to air, and in about a month was all of the same yellow colour. This oil was washed with water for some days to free it from picoline; when the smell of that base was no longer perceptible, a quantity of the oil was dissolved in hydrochloric acid; on addition of platinum chloride, a light buff-coloured precipitate, came down, which, under the microscope, was seen to consist of two different varieties of crystals. On ignition, it left 27·04 per cent. of platinum,

whereas a salt of the formula $C_{12}H_{14}N_2 2HCl PtCl_4$, would contain 33·05 per cent. It is evident that the oil consists of two substances; and I am at present engaged in effecting their separation, as one of these only volatizes with water-vapour. I hope ere long to be able to communicate the results of some experiments with this curious body.

Physiological Action. — In conjunction with Professor McKendrick, the physiological action of several substances described in this Journal for October 1876, and in this paper, have been ascertained. The results will form the subject of a more extended memoir; I shall give here, however, a short sketch of their action. Pyridine, picoline, lutidine, and their salts have a very slight action, apparently producing drowsiness. The methyl iodides of these bases are intense irritants to the cerebral centres, and produce paralysis of the fore limbs. The action is of the same kind, but even more intense, with ethyl and allyl derivatives. Dipyridine and dipicoline produce the same effect, but even more strongly; and when combined with methyl or ethyl iodide they are fearful poisons.

The ammonium salt of dicarbopyridenic acid proved to be a tremendous excitant, producing fits resembling epilepsy; curiously, its methyl ether had no appreciable effect. The general law appears to be that the more complicated the body the more energetic its action; but the effect also depends largely on the specific character of each substance.

XXXIII. *On the Diameter of the Wire to be employed in winding an Electromagnet in order to produce the Maximum Magnetic Effect.* *By* R. S. Brough*.

IN 1866 Mr. Schwendler investigated the best galvanometer resistance to employ in testing with Wheatstone's bridge, a question which was previously involved in complete obscurity, some physicists arguing that, since near balance the current passing through the galvanometer approaches the indefinitely small, therefore the number of convolutions, and hence the resistance of the galvanometer ought to be indefinitely great†.

I may here remark that Count du Moncel, in a communication to the Academy of Sciences, has unjustly criticised Mr. Schwendler's method of treating the subject of electro-

* Read before the Asiatic Society of Bengal on the 6th of April, 1877, and communicated by the Author.

† Philosophical Magazine, May 1866.

magnets*. The latter supposed the dimensions of the bobbins (as I also do in this paper) to be given, fixed, and immutable; while the learned Count starts with varying the depth of the bobbin, and piques himself on getting a larger magnetic effect out of it than Mr. Schwendler did. The best thickness of wire to wind on a given bobbin, and the best size and shape of bobbin to employ for a given purpose, are two totally distinct questions.

While investigating the above problem, the question of the influence of the insulating covering of the wire on the results occurred to Mr. Schwendler; and he went into it in a subsequent paper†.

Mr. Schwendler attacked the problem from the point of view of the resistance of the bobbin; but it seems to me that it yields more readily and presents a more definite result (the former method gives an equation of the fourth order, which has to be solved by a rather coarse approximation) when we start from the thickness of the wire. This method has also led me to a singularly simple relation existing between the resistance of the electromagnet and the external resistance.

I shall take the case of an elongated bobbin with straight sides and circular ends, because this is a very common form to give to galvanometer-coils, and because the results can at once be reduced to those applicable to circular bobbins by simply putting the length of the sides equal to nothing in the various expressions.

Let Y = the magnetic effect of the bobbin,
R = the resistance of the bobbin,
S = the external resistance,
E = electromotive force of the battery,
and n = the number of convolutions.

Then (Jacobi and Dub)

$$Y = \frac{nE}{R+S};$$

and the problem is to make Y a maximum‡, treating the diameter of the wire with which the bobbin is wound as the independent variable, of which n and R are known functions.

* *Comptes Rendus*, vol. lxxvi. pp. 368–371.

† Philosophical Magazine, January 1867.

‡ The force exerted by a coil on a steel magnet is proportional to Y, whereas the force exerted on a soft-iron armature is proportional to Y^2; but whatever value of the variable makes Y a maximum will also make Y^2 a maximum; so the one solution meets both cases.

Let A = the outer diameter of the circular ends,
a = the inner " " "
b = the length of the bobbin,
c = the length of the straight sides between the circular ends,
δ = the diameter of the wire,
ρ = the radial thickness of the insulating covering,
and L = the length of the wire on the bobbin.

Then

$$n = \frac{b(\mathrm{A}-a)}{2(\delta+2\rho)^2}$$

for each wire being allowed a square, the length of whose sides is equal to the diameter of the covered wire; and

$$\mathrm{L} = \frac{b(\mathrm{A}-a)}{2(\delta+2\rho)^2}\left\{\frac{\pi(\mathrm{A}+a)}{2}+2c\right\}.$$

But

$$\mathrm{R} = \lambda\frac{4\mathrm{L}}{\pi\delta^2},$$

where λ is the specific resistance of the conducting material of the wire, *i. e.* the resistance between opposite faces of the unit cube of the conducting material. Therefore

$$\mathrm{R} = \frac{\lambda b(\mathrm{A}-a)}{\pi\delta^2(\delta+2\rho)^2}\{\pi(\mathrm{A}+a)+4c\}.$$

We had

$$\mathrm{Y} = \frac{n\mathrm{E}}{\mathrm{R}+\mathrm{S}}.$$

Put

$$\theta = \frac{1}{\mathrm{Y}};$$

then

$$\theta = \left(\frac{\mathrm{R}}{n}+\frac{\mathrm{S}}{n}\right)\frac{1}{\mathrm{E}};$$

and it is required to make θ a minimum with respect to δ.

Now

$$\theta = \left(\frac{\lambda}{\pi\delta^2}\{\pi(\mathrm{A}+a)+4c\}+\frac{(\delta+2\rho)^2\mathrm{S}}{b(\mathrm{A}-a)}\right)\frac{2}{\mathrm{E}},$$

$$\frac{d\theta}{d\delta} = \left(-\frac{\lambda}{\pi\delta^3}\{\pi(\mathrm{A}+a)+4c\}+\frac{(\delta+2\rho)^2\mathrm{S}}{b(\mathrm{A}-a)}\right)\frac{4}{\mathrm{E}},$$

and

$$\frac{d^2\theta}{d\delta^2}=\left(\frac{3\lambda}{\pi\delta^4}\left\{\pi(A+a)+4c\right\}+\frac{S}{b(A-a)}\right)\frac{4}{E}.$$

Putting

$$\frac{d\theta}{d\delta}=0,$$

we have

$$\delta^3(\delta+2\rho)=\frac{\lambda b(A-a)}{\pi S}\left\{\pi(A+a)+4c\right\},$$

which equation expresses implicitly the value of δ which makes the magnetic effect a maximum.

Let us put $\frac{\rho}{\delta}=\mu$; then

$$\delta=4\sqrt{\frac{\lambda b(A-a)}{\pi(1+2\mu)S}\left\{\pi(A+a)+4c\right\}}.$$

This expression for δ contains μ, itself a function of δ; but a very simple artifice suffices to get over this difficulty. First suppose $\mu=0$, and solve the equation; the result will be an approximate value of δ, namely that which it would have were there no insulating covering to the wire.

Then, employing this approximate value of δ, calculate $\mu=\frac{\rho}{\delta}$, and recalculate the value of δ, using this value of μ.

By repeating this process, which involves very little trouble if logarithms be employed, any desired degree of accuracy may be attained.

From the above expression for δ we see that, so long as μ is not $=0$, the diameter of the wire (without its covering) will always be *less* than it would be were there no insulating covering.

The expression for the resistance of the bobbin may be written

$$R=\frac{\lambda b(A-a)}{\pi\delta^4(1+2\mu)^2}\left\{\pi(A+a)+4c\right\};$$

and supplying its value for δ^4, we find

$$R=\frac{1}{1+2\mu}S;$$

from which it is seen that, so long as μ is not $=0$, the

resistance of the bobbin must always be *less* than the external resistance. Putting $\frac{\rho}{\delta}$ for μ, we have

$$R = \frac{\delta}{\delta + 2\rho} S,$$

which expresses the physical law, namely that

$$\frac{\text{resistance of bobbin}}{\text{external resistance}} = \frac{\text{diameter of bare wire}}{\text{diameter of covered wire}}.$$

Alipore, Calcutta,
July 31, 1877.

XXXIV. *On Chemical Classification. By* M. M. Pattison Muir, *F.R.S.E., Assistant Lecturer on Chemistry, The Owens College, Manchester.*

[Concluded from p. 206.]

27. So far as actual experiments, taken in conjunction with the theory of valency and that of atom-linking, allow us to judge, it would appear that there is a close connexion between the valency of the atoms constituting a compound and the general properties, chemical as well as physical, of that compound, but that the position of the atom in the molecule also influences the character of the molecule. On this view it will be possible to regard the properties of a compound as functions (1) of the nature of the constituent atoms, and (2) of the manner in which these atoms are linked together. By the word "nature," as here used, is to be understood all those properties (atomic weight, density, valency, &c. &c.) which are inherent in the atom considered as an individual existence.

This view has much to recommend it, but as yet it can only be regarded as a good working hypothesis; adopting it as such, lines of work may be marked out, along which the researches of chemists may proceed for many years to come. We shall first require careful researches into the "nature" of the chemical atoms; this is an immense field. We shall then have another wide field for research in the circumstances which condition the valency of the atoms. The connexion between physical properties and valency, and many other questions, will be included in these two main lines of research. But while working in these directions in the past, and, I doubt not, while working in these directions in the future, chemists have ever and anon found the question, What *is* chemical energy? what do we mean by chemical affinity?

confronting them. I have almost ignored this question in the preceding paragraphs of this paper. Our knowledge of chemical action considered as a form of energy, is as yet almost *nil*. For the purposes of study it seems better to keep separate the questions, *What* is the structure of this or that body? and *Why* is the structure as it is? The first question relates to chemical statics, the second to chemical kinetics. The greater part of the labours of chemists has hitherto been devoted to attempting an answer to the first question. They have made some progress in the attempt; but there remains much to be done. When they shall have fully answered both questions, the science of chemistry will be complete. But that *when* is a long time off. Nevertheless, of each question it may be said, in the words of Lothar Meyer, "dass ihre Erforschung nicht nur möglich ist, sondern auch eine ausserordentlich dankbare Aufgabe für den menschlichen Forschergeist bildet"*.

28. I have thus endeavoured to give some kind of answer to the questions proposed at the close of paragraph 11, concerning the utility of that system of classification which is mainly founded upon the valency of the elementary atoms. This system does not, as yet, give us "a means for definitely settling the characteristics of each class;" it does not enable us, as yet, "to mark off class from class;" we cannot, as yet, "by its aid, correlate the leading characteristics of each class with the valency of the elementary atoms;" nor can we, as yet, "show a clear connexion between valency and chemico-physical properties of elements and compounds." A classification which might now be founded upon the valency of the elementary atoms would not fulfil the tests of a good system, as laid down in the first paragraph of the present paper. Nevertheless I think that I have succeeded in showing (or if I have failed, I think that the failure is due to want of clearness or of knowledge on my part, not to a deficiency in the facts themselves) that in the theory of valency, and in those subsidiary theories which are outcomes from it, we have a principle which is guiding research in directions in which valuable results have been already obtained, and in which we may confidently hope for yet better results in the future. I hope I have succeeded in establishing a large probability in favour of the belief that this principle will be one of the main foundations upon which a complete system of chemical classification will some day be raised; and at the same time I trust I have not altogether failed in representing

* *Die modernen Theorien*, 2nd ed. p. 149.

the difficulties which have yet to be overcome before this consummation is attained, and the dangers into which we run by rashly pushing to extremes deductions made from an hypothesis which is now but in its infancy.

29. Part of the general problem presented to the chemist of to-day is to trace the connexion which should exist (if the theory of valency be a true theory) between the properties of chemical compounds and the "nature" of their constituent atoms. In other words, the chemist is to examine the nature of the elementary atoms; he is to determine, with the greatest possible care, the physical and chemical constants of these atoms; he is then to endeavour to arrange them in groups, and he is to trace the influence of the individual atoms in conditioning the properties of their compounds. Turning, then, to the second part of the problem, the chemist is to pursue the inquiries already made into the structure of compounds; he is to endeavour to determine how the atoms are linked together in compounds, and he is to attempt to correlate this structure with the general properties of the compounds. He is then to combine both methods, and to ascertain, if possible, in what way the influence of the "nature" of the atoms is itself influenced by the linking of these atoms. He is then to study the transformations of energy which doubtless accompany all changes of structure; he is to inquire into the nature of chemical energy itself; and, finally, he is to combine the results of all his researches, and, aided by the laws of number and of space, he is to frame a complete system of chemical classification.

Now it is only within very recent years that that part of the general problem which deals with the connexion between the nature of chemical atoms and the properties of chemical compounds has received any careful investigation. In the remaining paragraphs of this paper I propose to give a brief sketch of what has been done in this direction.

30. Attempts have from time to time been made, throughout the preceding fifty or sixty years, to trace some connexion between the atomic weights of groups of elements and the general properties of the elements and their compounds.

Prout's hypothesis, advanced soon after the enunciation of the atomic theory by Dalton, is well known. The researches of Berzelius, of Marignac, and of Stas, showed that the hypothesis of Prout, in its original form at least, was untenable. Gmelin, in the 3rd and subsequent editions of his Handbook, drew attention to regularities in the increase and decrease of the atomic weights of analogous elements. Dumas, Glad-

stone, Cooke, Kremers, Pettenkofer, Odling, Newlands, and others extended the observed points of connexion between the atomic weights of the elements and their leading properties *.

But it is especially to Mendelejeff † that we owe a systematic attempt to correlate the leading properties, physical and chemical, of the elements with the atomic weights of these elements.

Lothar Meyer ‡ has also made important contributions to the same subject; and in his *Modernen Theorien* he has gathered together most of the facts which have been as yet established concerning the relations between atomic weights and properties of elementary substances.

31. The researches alluded to in the preceding paragraph allow us to say that a very large degree of probability has been established in favour of the hypothesis that the nature of the chemical elements is a periodic function of their atomic weights.

"We may define a periodic phenomenon as one which, with the constant and uniform change of the variable, returns time after time to the same value" §.

In the case before us we have as "variable" "atomic weight;" as "variant" we have the "nature of the chemical atom." In the present state of our knowledge we cannot define this variant with accuracy; hence it is not as yet possible, granting that the "nature of the chemical atom" is a periodic function of the relative weight of that atom, to state quantitatively the nature of this function. Nevertheless it may be possible to establish roughly that the general nature of the atom does vary periodically with the relative weight of the atom. It is necessary to break up the quantity "nature of the chemical atom," and to endeavour to show that such phenomena as specific volume, malleability, ductility, electric position, power of forming oxides, of forming chlorides, &c. &c. are really periodic functions of the atomic weights of the elementary atoms.

As I attempted to trace a connexion between physical properties of compounds on the one hand and chemical properties on the other, and the composition or structure of these compounds, so now would I endeavour to gather together a few of the facts which show that the physical properties of the elementary bodies vary periodically with the atomic

* See *Jahresberichte* for 1851 to 1865.

† *Ann. Chem. Pharm. Suppl.* Bd. viii. p. 133.

‡ *Ann. Chem. Pharm. Suppl.* Bd. v. p. 129, and *Suppl.* Bd. vii. p. 354, &c.

§ Principles of Science, vol. ii. p. 61.

weights of these bodies, and also that the chemical properties vary in the same manner.

32. If the specific volumes of the elements in the solid state (that is, the volumes occupied by masses proportional to the atomic weights of the elements) be arranged in order, beginning with that element which has the smallest atomic weight, and if these numbers be compared with the atomic weights of the elements so arranged, it will be seen that the former numbers increase and decrease periodically with the latter. Lothar Meyer has represented this fact graphically in the form of a curve. In the table annexed to the *Modernen Theorien* the atomic weights of those elements which exist at ordinary temperatures, or which can be obtained, in the solid state, are laid off in a horizontal line; vertical lines, representing the specific or atomic volumes of these elements, are also laid off; and a curve is drawn through the extremities of the latter lines. By noting some of the leading physical properties of the elements on this curve, Meyer shows to the eye the periodic nature of the connexion between the atomic weights of these elements and those properties. For instance, the atomic volume decreases from lithium through beryllium, and reaches a minimum in boron, from which it again increases through carbon, oxygen, and fluorine *, to sodium; the curve then passes downwards through magnesium to aluminium, where it again turns, and after passing through silicon, phosphorus, sulphur, and chlorine, reaches a second maximum in potassium, and so on. Lithium, sodium, potassium, rubidium, and probably cæsium, mark maxima in the curve of atomic volume. Boron, aluminium, cobalt, and nickel, rhodium, &c., mark minima in this curve.

The curve of atomic volumes shows also that elements with equal or nearly equal atomic volumes are possessed of very different properties, according as the element having the next greater atomic weight has a greater or a smaller atomic volume than that of the element in question. In other words, that if two elements have equal atomic volumes, but if one be situated on an ascending portion of the curve, its properties are very different from those of the other situated on a descending portion of the curve.

The more ductile metals are situated at the maximum and minimum points of the curve, or immediately follow the elements which are situated at these points. The more brittle

* For the method by which Meyer has made probable determinations of the atomic volumes of these elements, as also of hydrogen in the solid state, see *Ann. Chem. Pharm. Suppl.* Bd. v. p. 129 *et seq.*

metals are situated on the ascending portions of the curve, at no great distance from the points at which the minima are reached. An element whose atomic volume is greater than that of the element with the next smaller atomic weight is generally comparatively easily fusible, while an element having a smaller atomic volume than that of the element next below it in order of atomic weight, is fusible only with difficulty. The same relation holds between atomic volume and volatility of the elements. The ductile metals, whose position on the curve is at, or very near to, a maximum or minimum point, crystallize, as a rule, in the regular system ; those elements which are more brittle and more volatile, and are situated on ascending portions of the curve, crystallize for the most part in systems other than the regular.

The more volatile elements, which are placed on ascending portions of the curve, generally possess a greater coefficient of expansion by heat than those more fixed elements found at the minimum points of the curve. What we know concerning the refraction-indices of elementary bodies points to a periodic connexion between these numbers and the atomic weights of the same elements ; but our knowledge is as yet too limited to allow of any thing more than a general statement of such a connexion. The specific heats of the elements appear to bear some relation, not only to the atomic weights, but also to the atomic volumes of the elements. It would appear as if a certain magnitude must be attained by the atomic volumes of those elements which have small atomic weights before the law of Dulong and Petit is obeyed.

That the conductivity for heat and for electricity of metals varies periodically with their atomic weights is also apparent from a study of these three quantities.

The facts which I have now stated evidently point to a close connexion between atomic weight and general physical properties of the elements. The atomic weight may be regarded as a variable, and the physical constants of the elements as variants. Physical phenomena, says Meyer, must probably be regarded as functions, not only of space, of time, &c., but also as functions of the atomic weights of the elements exhibiting these phenomena, or of the elements constituting the compound bodies which exhibit these phenomena. Such a consideration offers a wide field for future physical determinations ; it also demands more exact atomic-weight determinations than have yet been made for many of the elements.

The elements may be roughly arranged in an electric series, wherein some are more positive, some more negative than

others. Now it is found that in the second and third sections of the curve of atomic volumes (that is, in those sections situated between the maxima lithium and sodium, and sodium and potassium) the elements situated on the descending portions of the curve are electro-positive, while those on the ascending portions are electro-negative. In the fourth, fifth, and sixth sections—the maxima being potassium and rubidium, rubidium and cæsium, and cæsium and bismuth—we find on each descending portion, first a set of electro-positive elements, then a set of electro-negative elements; then ascending towards the next maximum point, we have first electro-positive, and then electro-negative elements. But the electro-positive or negative character of those elements which are situated near a maximum point of the curve, is found to be much more marked, as a rule, than the electro-positive or negative character of those elements which are situated near a minimum point of the curve. Thus, in the fourth section of the curve, potassium and calcium are the electro-positive elements placed at and next to the maximum point; nickel and cobalt, copper and zinc, are the electro-positive elements placed at and immediately after the minimum point. Now the electro-positive character is much more marked in the case of potassium and calcium than in that of cobalt, nickel, copper, and zinc.

It would appear, then, that a well-marked positive or negative character is only possessed by those metals which have comparatively large atomic volumes; or, as it is expressed by Meyer, "the aggregation of a large mass in a small space appears incompatible with the development of a marked positive or negative character." A closer inspection of the position of the various elements in relation to their electro-positive or negative character shows that this character is much influenced, not only by the atomic volume of the individual element, but also by the manner in which the atomic volume changes from element to element. The electro-positive elements which are situated near a maximum point on the curve, and between whose atomic volumes there is a comparatively large difference, are more electro-positive in character than those situated near a second maximum point but possessed of atomic volumes between which there is a comparatively small difference.

Again, it is evident that the absolute magnitude of the atomic weight influences the positive or negative character of the elements. Thus, in the third section of the curve, on the ascending portion are found phosphorus, sulphur, and chlo-

rine, which are very electro-negative elements, forming well-marked oxyacids. In the fourth section, on the ascending portion of the curve are found arsenic, selenium, and bromine, also well marked electro-negative elements, forming oxyacids. In the fifth section, similarly placed to the preceding are tin, antimony, and iodine, which are again electro-negative, although to a less marked extent than either of the preceding groups of three. In the sixth section lead and bismuth occupy analogous positions to those occupied by antimony and iodine in section five; but lead and bismuth are possessed of but ill-defined negative characters. Now the differences between the atomic volumes of phosphorus, sulphur, and chlorine, especially between those of sulphur and chlorine, are considerable; but so are the differences between the atomic volumes of arsenic, selenium, and bromine, especially between those of the two latter elements. In this case, then, it would appear as if the less-marked negative character were to be traced to the larger atomic weights of the three elements as compared with those of the preceding three. It is also to be remarked that, while the whole of the elements in that period which includes phosphorus, sulphur, and chlorine are divided into but two groups, one of which is positive and the other negative, in the period which includes arsenic, selenium, and bromine there are four groups—first a positive, then a negative, then again a positive, succeeded finally by a negative group. The three elements in question are situated in the last negative group. Very probably the double change influences the properties of the whole of the elements in the complete period. The same considerations may be applied to the case of tin, antimony, and iodine. The differences between the atomic volumes are here smaller than in the two series we have just considered; the atomic weights of the elements are larger; and the elements form the second group of negative elements within one period. The negative properties of these elements are not so well marked as those of either of the preceding groups of three which we have mentioned. In the case of lead and bismuth, we have two elements situated somewhat similarly with antimony and iodine; but the difference between the atomic volumes of the two former is much less than that between the atomic volumes of the two latter; the atomic weights of lead and bismuth are very large; these elements occupy a position in the period succeeding the electro-positive elements mercury, thallium, &c., which again succeed the negative elements tantalum and tungsten. Now the negative character of bismuth is ex-

tremely slight. I have shown, in papers communicated to the Chemical Society, that the hydrates of this element are possessed of no acid properties. And this is what we should expect from a consideration of the position of bismuth in the periodic curve of Meyer. Further, the curve of the sixth section is almost certainly incomplete; there is a great gap between barium and tantalum. The determinations of the atomic weights of many members of this section also stand in much need of revisal. The next metal after bismuth, in order of atomic weight, is uranium (that is, if the number 240 be adopted for this metal). But the atomic volume of uranium places it much below bismuth on the curve. Is it not, then, very probable that a new element, or elements, is yet to be discovered with high atomic weight and comparatively low specific gravity, which will complete the section, the maximum point of which we can scarcely regard as occupied by bismuth?

The electro-positive or negative character of an element is evidently closely related to its general chemical deportment. Mendelejeff has shown that, if the elements be arranged in the ascending order of their atomic weights, the power of combining with oxygen possessed by the elements varies periodically with the atomic weight.

If the formulæ of the oxides be represented as containing two atoms of the element other than oxygen, then we find that, as the atomic weight increases, the amount of oxygen fixed increases by whole atoms, but that no element is capable of fixing more than eight atoms of oxygen to two atoms of itself.

Analogous periodic connexion may be traced between the atomic weights, the hydrides (or ethides), and hydrates of the elements, also between the atomic weights, oxides, and chlorides of the elements *.

The fact that the chlorides corresponding to certain oxides are unknown is one of considerable interest. Taking the nitrogen group of elements, for instance, we have the following oxides and chlorides. (These formulæ are not regarded as representing molecular weights.)

Oxides.

N_2O	N_2O_2	N_2O_3	N_2O_4	N_2O_5
—	—	P_2O_3	—	P_2O_5
—	V_2O_2	V_2O_3	V_2O_4	V_2O_5
As_2O (?)	—	As_2O_3	—	As_2O_5
—	Nb_2O_2 (?)	—	Nb_2O_4	Nb_2O_5
—	—	Sb_2O_3	Sb_2O_4	Sb_2O_5
—	—	—	Ta_2O_4	Ta_2O_5
	Bi_2O_2	Bi_2O_3	Bi_2O_4	Bi_2O_5

* See *Die modernen Theorien*, 2nd edit. pp. 330–334.

Chlorides.

—	—	$N Cl_3$ (?)	—	—
—	—	$P Cl_3$	—	$P Cl_5$
—	$V Cl_2$	$V Cl_3$	$V Cl_4$	—
—	—	$As Cl_3$	—	—
—	—	—	—	$Nb Cl_5$
—	—	$Sb Cl_3$	—	$Sb Cl_5$
—	—	—	—	$Ta Cl_5$
—	$Bi Cl_2$	$Bi Cl_3$	—	—

Each of these elements forms an oxide $X_2 O_5$; but these oxides are possessed of different degrees of stability, of fusibility, &c. $N_2 O_5$ is possessed of no great stability; it melts at a low temperature. $P_2 O_5$ sublimes unchanged at a red heat, but is entirely deoxidized by heating with carbon. $V_2 O_5$ is also easily reduced by heating in hydrogen, or in contact with carbon; it melts at a high temperature without decomposition. $As_2 O_5$ is reduced to $As_2 O_3$ by heat alone. $Sb_2 O_5$ is also reduced by heating; and $Bi_2 O_5$ loses oxygen at 150°. On the other hand, $Nb_2 O_5$ and $Ta_2 O_5$ neither melt nor volatilize, nor are they decomposed at a white heat. Niobic oxide becomes crystalline at a very high temperature; this oxide is also reduced by heating in hydrogen, while tantalic oxide is only reduced by contact with charcoal at a very high temperature. Now these two elements, which form the most stable and the least-easily reducible pentoxides, also form pentachlorides ($NbCl_5$ and $Ta Cl_5$) which are capable of existing in the state of gases. VCl_4 appears to be capable of existing for a time in the gaseous state. $P Cl_5$ and $Sb Cl_5$ are split up into $P Cl_3$ and Cl_2, and $Sb Cl_3$ and Cl_2, respectively, when heated. $BiCl_5$ does not exist.

Now, if we examine the positions of these eight elements upon the curve of atomic volumes and atomic weights, we find certain points of interest. Nitrogen is situated near a minimum-point; it is preceded and followed by electro-negative elements (carbon, oxygen, and fluorine); the differences between the atomic volumes of nitrogen and its immediate neighbours (assuming Meyer's numbers for the specific gravity of solid nitrogen, oxygen, and fluorine to be approximately correct) are not great; there is no well-marked electro-positive element in the neighbourhood of nitrogen. Phosphorus has a somewhat similar position in the third section of the curve; it is placed, however, further from the minimum-point than nitrogen; and right over against it, as it were, is the well-marked positive element magnesium: this element occupies the position on the *descending* portion of the curve

which phosphorus does on the *ascending*. Arsenic and antimony hold positions respectively in the fourth and fifth sections of the curve, somewhat similar to those occupied by phosphorus and nitrogen. But the fourth and fifth sections, as has been already pointed out, comprise each two minor sections within itself. Arsenic follows immediately upon a number of well-marked positive elements (cobalt, nickel, copper, and zinc). The influence of these appears to be exercised upon the negative arsenic. This is even more marked in the case of antimony. This element is immediately preceded by a long list of positive elements (rhodium, palladium, silver, cadmium, and indium), from which it is only separated by tin: it is followed by iodine. Bismuth is even more hemmed in, so to speak, by positive metals; the difference between its atomic volume and the volumes of its immediate predecessors in the curve is not great; and, so far as we know, it has no electro-negative element, such as fluorine, chlorine, bromine, or iodine (which respectively succeed nitrogen, phosphorus, arsenic, and antimony), coming after it. The absolute increase in atomic weight as we ascend from nitrogen to bismuth, also, it would appear, influences the power of these elements to combine with oxygen and to form stable oxides. The greater or less fusibility of the elements themselves and of their immediate neighbours must doubtless also be considered. Nitrogen is surrounded by gaseous elements, phosphorus by those which have low melting-points, arsenic by comparatively easily fusible elements, antimony by elements which are more fixed, and bismuth by elements of somewhat high melting-points.

Now if we turn to vanadium, niobium, and tantalum, we find that they are situated on *descending* portions of the curve, that, of the three, vanadium is nearest a minimum-point and nearest also to a number of positive elements. There is a very considerable distance between either niobium or tantalum and a positive element; and these metals are further protected on each side by the interposition of negative elements.

Considering these points (and others might be adduced), there is good ground for believing that the behaviour of the eight elements constituting the nitrogen group, towards oxygen and chlorine respectively, is closely connected, as a periodic function, with the atomic weights of these elements.

The position of the elements on the periodic curve is seen to be connected with the valency of these elements as deduced from a study of their gaseous chlorides, hydrides, ethides, &c. Thus the second and third sections of the curve are con-

stituted by the elements which are arranged in the following tables. The elements are placed in the ascending order of their atomic weights ; and over each is placed a figure representing its valency, so far as that has been with probability ascertained.

Section I.

1.	2.	3.	4.	3.	2.	1.
Li	Be	B	C	N	O	F

Section II.

1.	2.	3.	4.	3.	2.	1.
Na	Mg	Al	Si	P	S	Cl

Considerations such as those which were mentioned concerning the members of the nitrogen group may lead us to more determinate views concerning the valency of groups of elements. The eight elements belonging to the group in question form analogous oxides (nX_2O_5), some of which are more stable than others. Does it not appear very probable that the eight elements are really possessed of equal valency, but that the intensity, or the amount, of the chemical force exercised by each is different? We must never forget that the valency of an element and the chemical force exerted by that element are, in all probability, very different quantities.

If this view be adopted, the members of the nitrogen group must be regarded as pentads, and such compounds as PCl_3, $BiCl_3$, &c. as unsaturated compounds. Whether this be granted or denied, it is, I think, evident that the study of the general characters and analogies of compounds in the light of Mendelejeff's periodic law is calculated to throw considerable light on the general question of unsaturated compounds. (See par. 16.)

Mendelejeff has shown how the elements may be arranged in groups and in series in conformity with the gradual increase in their atomic weights. These groups may be again subdivided, and thus striking analogies and contrasts brought out between the members of the various groups. The remarks which I have already made illustrate the manner in which such divisions may be carried out. If the power of forming oxides, chlorides, hydrates, &c. be a periodic function of the atomic weights of the elements, we shall, when the nature of this function has been more studied, be in possession of an instrument whereby we may be able to arrive at a knowledge of the chemical composition or structure of groups of compounds. I have already attempted to show how a study of the general chemical reactions, and of the physical properties, of compounds, aids us in determining the

structure of these compounds. There is little doubt that the periodic law, when it is more fully developed, will be of equal service.

The arrangement of all the known elements in a series beginning with that element which has the smallest atomic weight, and regularly progressing through those having larger and larger atomic weights, and the connexion which is thus shown to exist between the positions of the elements and their general properties, lead us to believe that there are several gaps in this series which are yet to be filled by the discovery of new elements. Mendelejeff has even ventured to speculate regarding the properties of some of those elements; and it appears as if his predictions were to be realized in one instance at least. In this Magazine, for April, 1877, I have gathered together some of the facts which bear out Mendelejeff's idea that that metal which is the latest addition to the list of elementary bodies, really occupies the position assigned by him to a hypothetical element called eka-aluminium.

33. The "periodic law" evidently points to a quantitative connexion between the atomic weights of the elements and the chemical properties of these bodies and of their compounds. It is difficult to measure what we call "chemical properties;" and hence it is difficult to state the connexion which apparently exists in any other than a vague and indefinite manner. But the "periodic law" also enables us to connect together atomic weight and physical characters; and in each of these we have a quantity susceptible of very accurate measurement.

If we trace back the history of chemical theory, we find that chemists have ever been attempting to connect together in a definite manner a variable and a variant. In the early days of modern chemistry the variable was the elements which combine and the proportions in which they combine; the variant was empirical composition. A little later it was attempted to connect the empirical composition, as variable, with general chemical behaviour, as variant. I have endeavoured to show how chemists now attempt to connect atomic structure as the variant with the variable, composition—and also how they attempt to connect the latter, which they almost regard as synonymous with atomic structure, with physical properties as a variant. Mendelejeff's law presents us with a definite variable, viz. atomic weight; and it attempts to represent the physical and chemical properties, both of elements and compounds, as

functions of this variable. A further and more careful study of the exact properties of groups of compounds and of elements will doubtless enable us to make a nearer approximation to the nature of the function in question. Supposing that the periodic law be clearly established, we shall then be met with such questions as these :—Are there periods within periods? Is the divergence from the law itself periodic? and so on. The field for inquiry is evidently immense. Very many measurements must be made before we can attempt an answer to the simplest of the questions presenting themselves for solution.

It would not be difficult, perhaps, even now, to deduce some empirical mathematical expression which should appear to satisfy some of the results concerning the connexion of atomic weight and physical properties. If the measurements be accurate, such an empirical law may be generally easily enough deduced; but in a case so complicated as that presented to the chemist, an empirical law would be of little value; it would almost certainly be untrue. We must be content to wait for further researches, in the hope of being one day able to deduce a rational law which shall cover all the facts, and shall enable us to express, with a fair degree of accuracy, the nature of the function of which the chemical and physical properties of elements and compounds, and the atomic weights of the elements, are values.

In any attempts which may be made to solve this problem, it will be necessary to remember that most minds are biased in favour of a simple law, that we are ready to believe that Nature *must* be extremely simple in her working, whereas the facts which we certainly know all point to the extreme complexity of Nature's laws. Each more exact investigation shows that what we had before accepted as a full expression of the facts is but an approximation to such an expression. We are really dealing, as Prof. Jevons remarks, with phenomena made up of an infinite number of infinitely small units. It is only our incompetency to solve Nature's problems which obliges us continually to assume the phenomena to be much more simple than they really are.

It seems to me that a consideration of the infinity of the subject presented to the naturalist should prevent many of those unseemly controversies concerning pet theories which now and again disgrace the pages of works pretending to be devoted to an investigation of Nature.

Chemists are not wholly free from blame for the manner in which they incline to allow theories to usurp the place of

facts. But to endeavour to mend this mistake by declaring that science has no need of hypotheses appears to me to be but falling, if possible, into a worse error.

34. I have thus endeavoured shortly to trace the evolution of chemical theory in the past, and to indicate a few of the main lines along which, as it seems to me, it must proceed in the more or less immediate future. Although I have entitled this paper "On Chemical Classification," yet I have made no attempt at a system of classification: the time for such an attempt is yet, I believe, a long way off. We have, it is true, various systems, each, it may be, good in itself, and useful for certain limited purposes. But it is only when we shall have attained to a much wider knowledge of the connexions existing between composition and properties of chemical bodies that any attempt at a large scheme of classification likely to prove of lasting value need be made.

The three main lines of research (see par. 29) indicated in the foregoing paragraphs even now blend into one another; we cannot keep them altogether separate, if we would. The barriers between them are, of course, artificial, and merely set up as aids to research. Many subsidiary problems, not strictly included within any of these general questions, already present themselves, and will, in all probability, increase in number as investigation progresses.

A considerable number of exceptional phenomena are even now known, which are scarcely touched by any of our theories. Such, for instance, is the phenomenon of allotropism. We seem to have a vague idea of some kind connected with this word; but if a student were asked in an examination, "What are allotropic states?" and if he were to adopt the words of Prof. Stanley Jevons, and reply, "Curious states, which chemists conveniently dispose of by calling them *allotropic*, a term freely used when they are puzzled to know what has happened"*, he might be plucked; but on the question of allotropism he would be scarcely less ignorant than his examiner.

Exceptional phenomena form the nuclei around which researches, rich in fruitful work, must congregate. The science of Chemistry has made great advances in recent years; but it is now only entering on the exact stage of its history. Before that history can be completed much labour of head and hands is required; but it will be richly rewarded. "Viel Arbeit der Geister wie der Hände ist erforderlich, aber sie wird reichlich belohnt werden"†

* 'Principles of Science,' vol. ii. p. 341.

† *Die modernen Theorien*, 2nd. edit. p. 351.

XXXV. *On the Determination of Temperature-coefficients for Insulating Envelopes. By* THOMAS T. P. BRUCE WARREN, *Analytical Chemist to the India-rubber, Gutta-percha, and Telegraph-Works Company, Limited* *.

AT the Exeter Meeting of the British Association I read a paper on Electrification†, in which I endeavoured to show that the rate of variation in the insulation resistance of a core or cable under changes of temperature could be determined for any period of contact.

A statement was made in that paper which has led to the belief that india-rubber has the same constant for correcting from one temperature to another and for any period of contact. Professor Fleeming Jenkin, Mr. Latimer Clark, and others have pointed out that this phenomenon is not met with in gutta percha or any other insulator with which they are acquainted. This has led me to reexamine the matter, and to consider carefully the experimental data upon which the paper was founded.

The method of representing graphically the decrease of resistance due to increase of temperature corresponding to one minute's electrification can be followed out for two, three, or any number of minutes. In this way a series of logarithmic curves are obtained for any required duration of contact. These curves are generated by a constant which must first be ascertained by experiment for changes of temperature at the end of one, two, three, &c. minutes. This was omitted in the previous paper, or at least not dealt with as fully as the importance of the subject required.

The phenomenon of electrification, from what has just been pointed out, must appear to every electrician to have received additional importance, and no longer to be regarded as an unintelligible or inapplicable fact. One very important consequence of its being reducible to an intelligible variation is, that we can now calculate not only the changes in the resistance of an insulator due to variation of temperature, but we can ascertain with the same precision any required change due to prolonged contact at any required temperature.

The resistances at different temperatures under different durations of contact will, when tabulated, represent a series of logarithms, the base of each system being the ratio between

* Communicated by the Author, having been read in Section A of the British Association at Plymouth, August 1877.

† This paper was reprinted in this Magazine, December 1869.

the resistances for the same differences of temperature but corresponding to different periods of contact.

From these facts, electrification phenomena are capable of receiving a mathematical rendering which must prove of immense use to telegraph-engineers.

If the temperature-coefficient were constant for all and every period of contact, we should obviously obtain a series of curves with ordinates increasing in a constant ratio, which would mean that the ratio of the resistances for successive periods of contact did not diminish as we reach the higher temperatures. Now, as the temperature-coefficients for increased duration of contact diminish, the curves more nearly approach each other as the temperatures increase, which agrees with the fact that electrification-ratios are reduced less and less as the resistance itself diminishes.

A very curious result arises from this treatment of the subject, which I have not yet had sufficient time to examine, but may be mentioned here, as probably it may assist us to explain something of the nature of electrification.

To determine approximately the electrification-ratio, and consequently the resistance at any required temperature and for any period of contact. Calculate first the temperature-coefficient for the required temperature, which is simply the expansion of the ratio for 1° Fahr. to the power corresponding to the degrees of difference. Using this as the factor, extract the root of the ratio for any two given periods of contact; this will give very nearly the electrification-ratio corresponding to the same periods of contact at the required temperature.

It thus appears that electrification, which is an inseparable property of all insulators, follows some law of variation in which the temperature-coefficient of the insulator itself is a function.

I hope to have the pleasure of communicating at a future time the mathematical development of the application of logarithmic functions to electrification and thermal changes in insulating media.

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XXXVI. *On Binaural Audition.* *By* Silvanus P. Thompson, *B.Sc., B.A., Lecturer in Experimental Physics, University College, Bristol*.*

1. DURING the course of a series of experiments made a few months ago I had occasion to listen to a tone of slightly fluctuating pitch, the sound of which was led to one ear by a caoutchouc tube. Desiring to measure the pitch of the tone, it occurred to me to try to obtain interference-beats with a fork of very nearly the same pitch. Under the circumstances this could only be accomplished by holding the vibrating standard fork to the other ear. On doing this I was somewhat surprised to observe that the "beats" were heard with remarkable distinctness. Up to this time I was not aware of any experiments on the binaural estimation of beats, nor even that they could be so heard. Shortly afterwards I learned from Dr. W. H. Stone that he has been in the habit of using both ears, with a tuning-fork applied to each, in counting beats, and that he finds no difference between the result of this method and that of listening to both forks with one ear.

2. When two forks producing "beats" are thus applied, one to each ear, there is a possibility of the vibrations of the one fork being conveyed to the other ear exteriorly through the air. To eliminate as nearly as possible this chance I took two UT_3 ($c'=256$) forks, by Ducretet of Paris, and loaded one with wax to give about 2·5 beats per second when sounded with the other. The forks were unscrewed from their resonant boxes; an india-rubber tube was inserted into an aperture in the wall of each of the resonant boxes corresponding to the forks; and the two tubes were led to the two ears of the observer, and plugged round with cotton-wool. For the sake of greater precision, the tubes were led away from the apartment into two others, in each of which an assistant struck one of the forks and held it in front of the mouth of the resonant box. The "beats" were most distinctly heard, and seemed to be taking place within the cerebellum. When the forks vibrated so slightly as to be singly all but inaudible, the beats of the two were most distinctly heard.

3. When the beats were augmented in number per second by additional loading, they were still very distinct to binaural audition, and unusually harsh. On listening attentively for a combinational (difference) tone, none was observed. Two

* Communicated by the Author, having been read before the British Association, Section A, August 16, 1877.

forks, UT_3 and MI_3, which when struck or bowed together give a well-marked combinational tone, gave none when their sounds were separately led to the two ears. The same was the case with UT_3 and SOL_3. The effect was not entirely agreeable, being peculiarly harsh, yet unlike any ordinary discord. When MI_3 and SOL_3 were thus employed together, giving an interval of a minor third, no combinational tone was produced, but the effect was disagreeable and grating in the extreme—a most unpleasant jarring sensation being excited, apparently in the region of the top of the cerebellum. Several observers concurred in the absence of any combinational tone, and in the unpleasantness of the resultant sensation.

4. The next experiment was an attempt to ascertain the effect of bringing to the two ears waves of equal pitch and intensity, but differing in phase. A series of more elaborate experiments on this point is still in course of completion ; but before these were begun the following simple experiment was tried. One of my two UT_3 forks was loaded until it gave two beats per second with the other. When they were sounded together, there was obviously produced a rapid succession of all possible differences of phase. A slower succession of interferences was afterwards employed. When the two forks were presented separately (and simultaneously) to the two ears, and also when their tones were independently led to the ears by tubes as described above, it was still possible to recognize the fluctuations of tone. There was, however, no very decided weakening of the intensity of the sound comparable to the "silences" ordinarily observed between the "beats," the two tones seeming to be going on, but with a difference hardly definable in precise terms. When complete difference of phase was momentarily attained, there seemed to be a slight increase in the intensity of the sound, and the octave note (which, it will be remembered, is not amongst the upper partials of the fork) was faintly heard *. There was, however, no means of demonstrating the existence of such a tone, and the statement rests merely upon the evidence of the senses.

5. It is not easy to explain why interference-beats should thus occur in the simultaneous individual action of the two ears, while combinational tones (difference-tones) are inaudible. There is in the case of the auditory nerves, or

* It is of some importance to observe that in this experiment the forks were held by assistants, and detached from their resonant boxes, as described in No. 2.

portio mollis, no decussation like that of the optic nerves; the former do not intersect after leaving the fourth ventricle, in which they have their common origin, and from which they diverge right and left. There is in health a possible communication between the ears across the pharynx, through the Eustachian tubes. Moreover the bone of the skull itself is capable of conveying sonorous tremors, which might account for both ears hearing a sound entering by one only. In either of these latter cases, however, there would be no reason why combinational tones should not be equally audible in binaural as in monaural audition; so that we are driven to the hypothesis that any means of comparison which may exist in the nerve systems of the ears exists deep-seated in the actual structure of the brain. This may be the reason why dissonances are in binaural audition so excessively disagreeable, and why even ordinary consonant intervals become harsh. They evoke a discontinuous sensation when there is no opportunity of their blending previously to acting upon the sensitive mechanism of the nerve-structures. The discontinuity of the sensation produces an intensity of effect exceeding that of a continuous one. Hence sounds all but inaudible themselves may yield, as noted in No. 2, very well-marked beats, enabling the ear thus to detect the most delicate differences of tone. Thus, for example, I have, in a still room, hung up a fork with its resonant box, and, after exciting its vibrations with a bow, have made it swing like a pendulum at the end of a string. On retiring to the further end of the room, and listening to its tones with a resonator in the ear, I have, by holding to the other ear a fork vibrating accurately in unison with the first, been able to pronounce by the audible fluctuations of tone whether the swinging fork were advancing or retreating—that is to say, whether the motion of translation at any given moment were in the same direction as, or in an opposite direction to, the propagation of the sonorous waves.

XXXVII. *On the Magnetic Behaviour of Chemical Compounds.* *By* Professor G. Wiedemann.

[Concluded from p. 173.]

11. *Magnetisms of the Oxides of the Magnetic Metals.*—The oxides, having been heated to redness, investigated directly in the flat flasklet, show in general a much feebler magnetism than the corresponding salts or hydrates.

If the molecular magnetism of the salts is equal to μ_s, the magnetism μ_o of the oxides is :—

Manganous oxide	$\mu_o = 0{\cdot}31\mu_s$
Nickelous oxide	„ 0·47
Didymic oxide.....	„ 0·52
Cupric oxide	„ 0·21
Ferric oxide.....	„ 0·13
Ferric oxide with alumina *	„ 0·55
Chromic oxide.....	„ 0·35
The same after strong incandescence	„ 0·39
The same with alumina *	„ 0·56

Therefore the molecular magnetism of the burnt oxides is much less than that of the corresponding salts and hydrates ; it varies also according to the manner of exhibition and treatment of the oxides. From the behaviour of the mixtures of ferric and chromic oxides with alumina it follows that when the coagulation of individual particles of the magnetic oxides is prevented by the presence of an indifferent substance, their magnetism turns out greater. This may arise from the enhancement of the molecular forces that hold the magnetic atoms of metal in their relative position and prevent their rotation, occasioned by the condensation with the heating, being considerable ; and in that case, with a finer division, the demagnetizing mutual action of the parts lying side by side is as much weakened as the magnetizing action of those situated one behind another. Since in certain cases the former is greater than the latter, this distribution may effect an increase of magnetism. Whether moreover the diminutions of magnetism here observed are to be attributed only to the considerable alterations of density, or are connected with an actual change in the atom-grouping, cannot at present be decided.

12. *The Hydrates of the Superoxides* of manganese, cobalt, and nickel have only a very feeble magnetism ; it is different with the magnetism of the so-called *superoxide of chromium*, CrO_2. The round glass vessel was filled first with a solution of chromic sulphate, and then with one of bichromate of potass, and each time the magnetism determined ; in the second case it was nearly equal to that of water, therefore negative. Afterwards the glass was partly filled with the first, and then filled up to the mark with the second solution, and the magnetism again

* The ferric and chromic oxides were, for these experiments, precipitated jointly with the alumina from a mixed solution of ammonia-alum and ferric chloride or chromic nitrate, and the mixture afterwards heated to incandescence.

determined. Calculated for the atom of the chromium contained in the chromic-sulphate solution, it was found nearly equal to the atomic magnetism of chromium in the ordinary chromic salts. Thus the magnetism of the total chromium

(1) in the solution of chromic sulphate 54·2
(2) in the mixture . . . . . 23·1

The weights of chromic oxide in the two were as 23·62 : 11·30 = 1 : 0·47, the magnetisms as 1 : 0·43. Therefore the magnetism of the chromium oxide was not essentially changed with the precipitation. Accordingly the so-called superoxide of chromium is a saline combination of chromic acid with chromic oxide, as, indeed, it is also well known that by washing it with water it can be more and more decomposed into those two constituents.

13. *Magnetism of the precipitated Metallic Sulphides.*—While magnetic pyrites exhibits strong magnetism, in the precipitated sulphides of the metals this is very little. For the investigation the solutions of the salts of the magnetic metals, in weighed quantities, in the glass vessel of the torsion-apparatus, were precipitated by a solution of sulphide of ammonium. It was then found that if, as above, μ_s is the molecular magnetism of the dissolved salt, that of

Sulphide of manganese $\mu_\sigma = 0{\cdot}27\,\mu_s$
„ iron . . 0·05
„ cobalt . . 0·04
„ nickel . . 0·04

These considerable differences cannot also be referred to an alteration of density; much rather may it be safely assumed that the magnetic atom-group in the sulphides of the metals is another than that in the oxygen and haloid salts and in the hydrates.

14. *Ferric and Ferrous Oxalate of Potass.*—By the determination of the molecular magnetism of these two salts, of which the former (contrary to the rest of the ferric salts) is green, while the latter is yellow, it can be forthwith demonstrated that ferric oxalate of potassium possesses the molecular magnetism of the peroxide salts, and the ferrous oxalate that of the rest of the salts of the protoxides. Accordingly an assumption of Haidinger's (Pogg. *Ann.* vol. xciv. p. 246, 1855), that the former salt, optically regarded, contained ferrous carbonate, cannot be maintained.

15. *Modifications of the Salts of Chromic Oxide.*—When a violet solution of chrome-alum is heated till it assumes a green colour, after the cooling its magnetism remains the same as

before the transformation. Therefore the change of colour cannot arise from a possible separation of colloid oxide of chromium from the salt, which, like the colloid oxide of iron, would exhibit a lower degree of magnetism than the oxide combined with the acid.

16. *Magnetism of the Cyanides of the Magnetic Metals.*—The precipitates obtained in the flask of the torsion-apparatus by adding hydrocyanic acid to the salts of acetic acid, of cyanide of nickel and cyanide of cobalt, possess a much lower magnetism than the corresponding oxygen and haloid salts. If the former be denoted by μ_{cy}, the latter by μ_s, then with

Cyanide of cobalt $\mu_{cy} = 0{\cdot}60\text{–}0{\cdot}65\,\mu_s$,
Cyanide of nickel $\mu_{cy} = 0{\cdot}45\,\mu_s$.

When the precipitates are dried, the molecular magnetism of the cobalt cyanide remains nearly constant, that of the nickel cyanide rises to about $0{\cdot}63\,\mu_s$.

While the simple cyanides of the magnetic metals still show a not inconsiderable amount of magnetism, this diminishes to a great extent or quite vanishes when those metals enter into combination with cyanogen in other atomic groupings. Thus, as Faraday showed, ferricyanide of potassium is only feebly magnetic, and ferrocyanide of potassium is even feebly diamagnetic, although the latter salt contains more iron in its molecule than the former. Correspondingly, also, in these salts the iron cannot be directly demonstrated by the ordinary reagents.

The mangani- and cobalticyanides of potassium behave altogether similarly to the ferricyanide. According to former experiments the molecular magnetism of these salts, as well in solution as in the solid state, is the following:—

	Dissolved.	Solid.
Manganicyanide of potassium .	30·5	31·9
Ferricyanide of potassium . .	16·1	15·7
Cobalticyanide of potassium . .	...	−0·75

Here also the molecular magnetism of the iron-salt is the mean between those of the manganese- and the cobalt-salt. In comparison with the magnetism of the protoxide salts it appears diminished in an approximately equal proportion:—

$100{\cdot}4 - 31{\cdot}2 = 69{\cdot}2$; $83{\cdot}1 - 15{\cdot}9 = 67{\cdot}2$; $67{\cdot}2 + 0{\cdot}75 = 68$.

The behaviour is therefore the same as if to the magnetic radicals a strongly diamagnetic radical, with the diamagnetism belonging to it, were added.

A further insight into the constitution of the ferro- and

ferricyanides &c. is afforded by the experiments described at p. 170, and by others similar to them. By those experiments it is proved that when a solution of these salts is mixed with the solution of a salt of iron, nickel, cobalt, or manganese, and thereby the potassium in them is partially or entirely replaced by the magnetic metals of the latter, the molecular magnetism is augmented by the magnetism of those metals—as, *e. g.*, on the replacement of the potassium in the chloride of potassium by the same metals, in which the magnetism of the potassium is a vanishing quantity against that of the latter. The *electrolytic* behaviour shows that the ferro- and ferricyanides and the analogous salts of manganese and cobalt are to be regarded as compounds in which the one constituent (*e. g.* the potassium) is electrolytically opposed to the radical combined with it (ferrocyanogen &c.) in like manner as the chlorine in potassium chloride. It results from the *magnetic* investigation that, even in the *undecomposed* salts, the potassium in the ferrocyanide &c. possesses altogether the same properties as in the chloride of potassium &c. The constitution of both series of salts is in this respect the same; the former are therefore, like the latter, to be considered, even in the *undecomposed* state, as binary compounds.

It is remarkable that also the combined cyanides of nickel and potassium ($NiCy_2 + 2\,KCy$), which possesses a composition deviating from the constitution of the ferrocyanides, is feebly diamagnetic. Consequently this salt is not to be imagined a double salt; much rather, as results from its electrolysis, may the potassium be opposed as electropositive radical to the total remaining complex of atoms as electronegative radical.

A quite different behaviour is exhibited, according to more recent experiments, by the so-called potassium *chromicyanide* ($CrCy_3 + 3\,KCy$), although it appears to be composed after the analogy of the potassium ferricyanide &c.; and it is just the same with the potassium *chromisulphocyanide*. If we denote by G the weight of the magnetic metal contained in the solutions of these salts (which was partly determined directly, and partly calculated from the weight of the salt present in the solution), by M the magnetism of the solutions after deducting the (negative) magnetism of the glass filled with water, we obtain the magnetism α for each atom of the magnetic radical for:—

	G.	M.	α.
Potassium chromicyanide ...	0·8273	0·3178	42·0
„ ferricyanide	0·9734	0·1329	15·9
Ferric nitrate	0·5286	0·4532	100·0

In the investigation of the powdered solid salts simultaneously with the solution of the ferric nitrate in the flat glass vessel, there was obtained for

	G.	M.	α.
Potassium chromicyanide	0·511	2800	42·7
„ ferricyanide.....	0·606	1120	15·4
Ferric nitrate	0·918	1105	100·0
Potassium chromisulphocyanide	0·2525	2825	41·1
Solution of normal ferric chloride	0·1226	3095	100·0

According to this the magnetism of the chromium in the potassium chromicyanide (42·7) and in the potassium chromisulphocyanide (41·1) is nearly the same as that of the rest of the chromic-oxide salts (41·9); there is no such diminution of it to be perceived as that which is conditioned by the atomic grouping belonging to the ferricyanide. We should hence be justified in considering the potassium chromicyanide and chromisulphocyanide simple double salts in which chromium possesses quite the same properties as in solution of chromic chloride, for instance, &c.

17. Of great interest is the magnetic deportment of a series of *ammoniacal compounds of cobalt*, *nickel*, *chromium*, and *copper*. As is known, chemically the so-called ammonio-cobalt salts behave differently from the ordinary salts of cobalt; and one is inclined to assume that in them the cobalt occupies the place of a part of the hydrogen of the ammonium. Other ammoniacal compounds of cobalt, *e. g.* the double salt ammonio-cobaltous sulphate &c., on the contrary, range themselves perfectly with the ordinary cobalt-salts. The same differences are shown also in the magnetic behaviour of the various cobalt compounds; and the latter is accordingly adapted, in doubtful cases, to decide concerning their constitution.

Nearly the same molecular magnetism is possessed by the double salts ammonio-cobaltous sulphate &c., and by the ammoniacal compounds obtained by passing gaseous ammonia over anhydrous cobaltous sulphate, cobaltic chloride, &c., as by the ordinary oxygen and haloid salts of cobalt. Thus, after deducting the magnetism of the glass filled with water, retaining the previous notation, there was found:—

	G.	M.	α.
$CoSO_4 + (NH_4)_2SO_4 + 6\,aq$ ...	0·4678 Co	86·6	73·0
$CoSO_4 + 6NH_3$	0·1439 Co	22·3	64·7
Normal ferric chloride	0·1226 Fe	30·9	100

More or less deviating from this is the behaviour of those

compounds which arise from oxidation of ammoniacal solutions of cobaltous oxide. The magnetic moments of a series of them, as well as of the compounds obtained by precipitation from cobaltous salts by nitrites, are obtained from a series of observations in which the dry salts and an acid solution of ferric chloride were examined in the flat flask. The salts were presented partly by Erdmann, partly by Künzel. From these observations it follows, still retaining the same notation, that:—

	G.	M.	α.
(1) Diamine cobaltic sulphite ($4NH_3$, Co_2O_3, $3SO_2$, $5H_2O$)	0·4689 Co	14·7	14·8
(2) Triamine cobaltic sulphite ($6NH_3$, Co_2O_3, $3SO_2$, H_2O)	0·3178 „	20·6	26·0
(3) Acid pentamine cobaltic sulphite ($10NH_3$, $2Co_2O_3$, $6SO_2$, $9H_2O$)	0·6151 „	29·5	23·1
(4) Tetramine cobaltic hyposulphate ($8NH_3$, Co_2O_3, S_2O_5)	0·2792 „	0·2	0·32
(5) Diamine cobaltic nitrite and ammonium nitrite ($4NH_3$, Co_2O_3, $3N_2O_3$)+2(NH_4NO_2)	0·5773 „	0·52	0·4
(6) Triamine cobaltic nitrite ($6NH_3$, Co_2O_3, $3N_2O_3$)	0·4444 „	2·04	2·2
(7) Roseocobaltammonium nitrate ($10NH_3$, Co_2O_3, $3N_2O_5$)	0·3658 „	−0·09	−0·12
(8) Basic pentamine cobaltic nitrate ($20NH_3$, $2Co_2O_3$, $5N_2O_5$)	0·2914 „	+0·08	0·13
(9) Oxycobaltammonium nitrate ($5NH_3$, CoO_2, N_2O_5, H_2O)	0·4585 „	0·37	0·38
(10) Purpureocobaltic chloride ($10NH_3$, Co_2Cl_6)	0·5768 „	−0·54	−0·46
(11) Luteocobaltic chloride ($12NH_3$, Co_2Cl_6)	0·4925 „	−0·11	−0·10
(12) Potassiocobaltous nitrite from a neutral solution ($3CoO$, $3K_2O$, $6N_2O_3$, H_2O)	0·5538 „	11·8	10·1
(13) Potassiocobaltic nitrite from an acid solution (Co_2O_3, $3K_2O$, $6N_2O_3$, $3H_2O$)	0·2458 „	2·8	5·3
(14) Ammonio-potassio-cobaltic nitrite (Co_2O_3, $4NH_3$, K_2O, $4N_2O_3$)	0·4143 „	3·2	3·5
(15) Ferric chloride up to the higher mark	0·1244 Fe	27·8	100
(16) The same filling only the bulb	0·1022 „	26·8	100
(17) Potassio-calcio-cobalt nitrite (CoO, CaO, K_2O, N_2O_3)	0·3620 Co	8·3	9·5
(18) Potassio-strontio-cobalt nitrite (CoO, SrO, K_2O, N_2O_3)	0·3135 „	7·0	9·5
(19) Potassio-baric cobalt nitrite* (CoO, BaO, K_2O, N_2O_3)	0·3313 „	8·8	11·1
(20) Ferric chloride	0·1226 Fe	30·9	100

While the three first-mentioned amine salts still preserve a not inconsiderable temporary magnetism, this is very small with the other salts; nay, some of them, as *e. g.* Nos. 7, 10,

* The formulæ are supposed to represent merely empirically the composition of the compounds.

and 11, are even diamagnetic. We must therefore assume that in the latter salts the cobalt is combined in a quite different manner from that in which it is in the ordinary cobaltous salts or those analogous to the ferric salts. Much rather may these salts, exactly like the ferrocyanides, contain the cobalt in a special scarcely magnetic group, while perhaps the cobalt replaces a portion of the hydrogen of the ammonium. For the first four salts Geuther* had put forth the opinion that they were double salts which contained respectively, together with one molecule of luteocobaltammonium sulphite, either (1) two or (2) one molecule of cobaltic sulphite, or (3) with one molecule of sulphite of roseocobaltammonium one molecule of cobaltic sulphite, or, finally, (4) with two molecules of hyposulphate of luteocobaltammonium one molecule of basic cobaltic hyposulphate.

The formulæ of the salts 1 and 4 would therefore have to be multiplied by three, that of salts 2 and 3 by two. They would contain (1) six, (2 and 3) four, and (4) six atoms of cobalt; and their molecular magnetism would be respectively:—(1) 88·8, (2) 104, (3) 92·4, (4) 1·92. The luteocobaltammonium sulphite (in analyzed formula $12\,NH_3$, $Co_2\,O_3$, $3\,SO_2$) and roseocobaltammonium sulphite ($10\,NH_3$, $Co_2\,O_3$, $3\,SO_2$), as well as the hyposulphate of luteocobaltammonium ($12\,NH_3$, $Co_2\,O_3$, $2\,S_2\,O_5$, $H_2\,O$), contain two atoms of cobalt each. Since, further, the luteo- and roseocobaltammonium salts are to be considered almost unmagnetic, the total magnetism of the double salts would fall to the cobaltic sulphite and hyposulphate only. The magnetism of each atom of cobalt contained in the latter would accordingly be (1) 22·2, (2) 52, (3) 46, (4) 0·48. But these atomic magnetisms deviate considerably from one another; only salts 2 and 3 could contain a common magnetic group of atoms. At any rate the cobaltic salt to be assumed as existing in the salts could not be considered after the analogy of the ordinary ferric salts, since then the magnetism of the cobalt contained in them must be greater than in the cobaltous salts (67·2).

The yellow precipitates obtained by adding to neutral or acid solutions of cobalt-salts nitrite of potass showed themselves by their magnetism to be essentially different from the ordinary cobaltous salts, as well as from the first-mentioned salts (1–3); and so did the nitrites of cobalt which at the same time contained barium, strontium, or calcium (17, 18, 19). The magnetism of the latter is nearly the same as that of the so-called potassio-cobaltous nitrite precipitated from a neutral

* *Jahresb.* 1863, p. 267; Erdmann's *Journ.* vol. xcii. p. 32.

solution (12); so that to these salts a common structure, but one essentially different from the constitution of the ordinary cobaltous salts, may be attributed.

With the *nickel salts* no such anomalies are exhibited. Thus, *c. g.*, there was obtained for the following salts:—

	G.	M.	α.
$NiO, 2K_2O, 3N_2O_3$	0·5117	29·7	27·4
$NiO, BaO, K_2O, 3N_2O_3$...	0·4224	24·9	27·9
$NiO, SrO, K_2O, 3N_2O_3$...	0·4088	25·5	27·9
$NiO, CaO, K_2O, 3N_2O_3$...	0·3919	23·4	28·2
$NiSO_4, 4NH_3, 2H_2O$	0·5021	30·9	28·9
$NiO, N_2O_3, 4NH_3$	0·8341	59·9	29·1
Ferric chloride.....	0·1244	27·1	100

From previous investigations the following is the magnetism of the atom of nickel in the salts

	α.
$NiSO_4, 4NH_3, 2H_2O$	29·1
$Ni(NO_3)_2, 4NH_3, 2H_2O$	28·0

Considering the number of diamagnetic substances which, especially in the four salts first mentioned, are combined with nickel, the diminution of the magnetism, compared with that of the ordinary nickelous salts (30·5), may not be too great. Therefore we cannot assume that the nitrous double salts of nickel, similarly to the cobalt salts with a perfectly analogous composition, possess a constitution essentially different from that of the ordinary nickelous salts; much rather do they at once connect themselves with the latter. Finally, in the ammoniacal salts of nickel the ammonia may, as in the analogously composed cobalt-salts, be attached, like water of crystallization, to the unaltered protoxide salts merely by a molecular union.

The same behaviour is exhibited (as I have previously shown) by the *ammoniacal copper-salts*. The atomic magnetism of the copper in them came out as follows:—

	α.
Dissolved cupric salts	10·8
$CuSO_4, 5NH_3$	9·3
$CuSO_4, NH_3$.....	9·7
$CuSO_4, 4NH_3, H_2O$	9·0
$CuSO_4, 2NH_3$	9·6
$CuCl_2, 2NH_3$	10·1
$CuBr_2, 2NH_3$	9·8

According to this the view of Graham *, that copper replaced

* *Ann. d. Chem. u. Pharm.* vol. xxix. p. 29.

a portion of the hydrogen of the ammonium group, and consequently the salts were composed similarly to the cobalt-ammonium salts, and therefore perhaps

$$CuSO_4 + 2NH_3 = \begin{matrix} N \\ N \end{matrix} \begin{matrix} H_3 \\ Cu, \\ H_3 \end{matrix} SO_4,$$

$$CuSO_4 + 5NH_3 = CuSO_4 + \begin{matrix} N \\ N \end{matrix} \begin{matrix} H_3 \\ CuSO_4 + 3NH_3, \\ H_3 \end{matrix}$$

represented their composition, is untenable. It is much more probable that here also the ammonia, similarly to water of crystallization, attaches itself to the unaltered group of the cupric salt.

The peculiar violet compound obtained when freshly precipitated chromic oxide is dissolved in ammonia, and the solution, mixed with excess of hydrochloric acid, slowly evaporated to crystallization, is sometimes regarded as the salt of a proper chromium base similar to the platinum bases, as *tetramine chromic chloride* $Cr(NH_3)_4Cl_3 + H_2O$. The magnetic investigation of the solid salt gave the following results:—

	G.	M.	α.
Ammonio-chromic chloride ...	0·6492	61·8	42·4
Ferric chloride	0·1244	26·1	100,

while the atomic magnetism of the chromium in the ordinary chromic salts is equal to 41·9. Hence in ammonio-chromic chloride the chromium exhibits the same deportment as in the chromic salts. Here, too, we cannot assume that the atom-group containing the chromium is essentially other than in the latter; and we are compelled to attribute to the ammonia a similar part as to the water of hydrates—precisely as in the ammoniacal nickel- and copper-salts. The formula of the salt should accordingly be written:—$Cr_2Cl_6, 8NH_3, 2H_2O$.

18. *Dissociation.*—It is known that a number of ferric salts in their solutions undergo dissociation, at a lower or higher temperature, into colloid ferric oxide and acid. We have already (p. 172) mentioned that by the determination of the magnetism of these salts their partial dissociation can be quantitatively verified. If m_0 is the magnetism of unit weight of iron in the solid salts or in those present in a very acid solution and not dissociated, m_1 the magnetism of unit weight of iron in the colloid solution of ferric oxide, m the magnetism of unit weight of iron in the solution of a partially dissociated salt in which the quantity of the ferric oxide combined with the acid

is to the colloidally dissolved free oxide as $1-x : x$, then is

$$m = m_0(1-x) + m_1 x.$$

Since the magnetism m_1 of the colloid ferric oxide is only 0·2198 of the magnetism m_0 of the oxide in combination with acid, therefore

$$x = 1{\cdot}28\left(1-\frac{m}{m_0}\right).$$

Consequently by determining the magnetism we can directly determine the ratio $x : 1$ of the quantity of ferric oxide dissociated to the total quantity of it in the salt.

In this manner the magnetism of the unit weight of iron in variously dilute solutions of ferric chloride was observed, with the following results:—

Series I.			Series II.	
Iron in 10 c. c. of solution. grm.	m_1.	$(1-x)\,100$.	Iron in 10 c. c. of solution. grm.	$(1-x)\,100$.
1·606	99·6	100	1·491	100·8
1·207	101·7	100	1·119	99·5
0·806	98·7	98·4	0·747	98·0
0·404	94·8	97·6	0·375	95·1
0·202	93·1	93·4	0·184	93·6
0·138	91·3	91·1	0·129	91·5
0·071	102·1	88·4	0·062	88·8

In the experiments of series II., 3·1 per cent. more of the ferric oxide than corresponded to equivalence with the acid present (according to the analysis of the most concentrated solution) was already contained in the colloid state. Therefore dissociation in ferric-chloride solutions proceeds slowly with increasing dilution.

The case is different with *neutral* solutions of *ferric sulphate* ($Fe_2(SO_4)_3$). In them the magnetism of the iron atom is perhaps only 80 per cent. of that of the atom of iron in very acid solutions of ferric chloride. The ratio hardly changes even when the iron contained in the solutions varies from 0·567 to 0·073 gram. in 10 cubic centims. From this it is calculated that about 25 per cent. of the salt in the solutions has become dissociated into colloidally dissolved ferric oxide and sulphuric acid, and only 75 per cent. of the total quantity of the ferric oxide and sulphuric acid remain combined with one another.

If a solution of *ammonium iron-alum* be investigated as to its magnetism, it is found that the ferric sulphate contained in

the alum, quite independently of the presence of the sulphate of ammonium, is dissociated, as when by itself, to the amount of 25 per cent. It is consequently in the highest degree probable that the iron-alum in the solution is completely decomposed into alkaline and ferric sulphates.

In a solution of *ferric nitrate* which in 10 cubic centims. contained 0·266 gram of iron, and to one eq. of Fe_2O_3 0·73 eq. of 3 N_2O_5 (being therefore basic), according to the magnetic investigation about 32 per cent. of the total amount of iron was dissolved as colloid ferric oxide. This proportion was increased to only 36 per cent. on diluting the solution to three times its original quantity.

Solutions of *ferric acetate* exhibit a dissociation far stronger still. In a neutral solution containing 0·182 gram. of iron in 10 cubic centims. nearly 70 per cent. of the total ferric oxide was in the colloid state; in neutral solutions of ferric tartrate about 57 per cent. of the salt is dissociated, and so forth.

19. *Combining-proportions of Acids and Bases.*—If to one equivalent of ferric oxide different quantities of dilute sulphuric acid be put, with increase of the latter continually greater quantities of ferric oxide enter into combination, as may be calculated direct from the magnetism of the unit of weight of iron in the solutions.

If we write neutral ferric sulphate $Fe_2, 3SO_4 = feO\,SO_3$, and if the ratio of the equivalents fe and SO_3 is as stated in the following Table, the percentages of the dissociated ferric oxide are those specified under x. Dividing the values $100-x$, consequently the percentages of ferric oxide which have combined with the acid to form salt, by the total number of equivalents of acid employed in the experiment, we obtain the values specified under y, which therefore indicate the number of equivalents of ferric oxide taken into combination by each equivalent of acid in the solution, thus:—

I.

Iron contained in 10 cub. centims. gram.	fe : SO_3.	x.	y.
0·343	100 : 73·4	58·7	0·56
0·339	85·1	37·9	0·73
0·334	98·6	26·9	0·74
0·329	111·5	14·5	0·76
0·325	122·8	12·2	0·71
0·315	146·6	8·3	0·63
0·304	182·8	5·9	0·51
0·293	219·6	1·9	0·45

II.

Iron contained in 10 cub. centims. gram.	fe : SO_3.	x.	y.
0·603	100 : 75·9	53·2	0·62
0·589	84·0	45·2	0·65
0·577	92·6	33·2	0·72
0·566	99·6	25·5	0·75
0·560	103·8	19·6	0·77
0·554	108·2	18·4	0·75
0·540	117·6	13·8	0·71
0·515	135·2	10·7	0·66
0·494	153·1	7·4	0·60

From these observations it follows:—

(1) If to a watery solution of colloid ferric oxide in a little sulphuric acid continually larger amounts of hydrate of sulphuric acid be added, the quantity of ferric sulphate in the solution gradually increases, while a portion of the colloid oxide and a part of the sulphuric acid persist uncombined beside it. *Even when the quantities of sulphuric acid and ferric oxide correspond to the same number of equivalents*, only about 75 per cent. of them are combined, while 25 per cent. *of the equivalents of sulphuric acid and ferric oxide are free in the solution.* If the amount of sulphuric acid is less than corresponds to one equivalent of the dissolved ferric oxide, then the quantity of ferric sulphate formed increases at first somewhat more slowly than corresponds to the accession of sulphuric acid, then gradually approaches a maximum; so that half an equivalent of acid added to the solution besides the first engages about 15 per cent. more, a further half-equivalent about 4 per cent. more, of the equivalent of ferric oxide. On employing about 4 equivalents of sulphuric acid to 1 equivalent of ferric oxide, nearly all the oxide combines with the acid; the maximum is so nearly reached that the deviation from it is covered by the errors of observation.

(2) With variation of the water-content of the solutions, whether the same number of equivalents of ferric oxide and sulphuric acid or different proportions of them be employed, the proportion of the ferric sulphate formed, on the one hand, and of the free acid and free oxide, on the other, do not change very considerably. From this proposition, if it may be extended beyond the limits of the experiments, it follows directly that, if on the employment of equal numbers of equivalents of base and acid the salt formed were insoluble (instead of being soluble like ferric sulphate), after the separation of the formed

portion of it from the remaining quantity of free base and acid, nearly the same percentage would again combine to form a salt as before. This portion would also be precipitated; and the process would go on in the same manner, until all the base and acid had combined and formed an insoluble salt.

(3) On employing increasing quantities of acid to 1 equivalent of ferric oxide, the amount of *free* acid in the solution first diminishes until the total quantity of the (free and combined) acid in the solution amounts to somewhat more than one equivalent. With a further increasing total quantity of acid in the solution the amount of the free acid increases.

(4) If we divide the quantity of ferric sulphate formed when one equivalent of ferric oxide is employed, by the number of equivalents of acid used, we obtain the remarkable result, that *the amount of ferric oxide combined with the same quantity* (1 *eq.*) *of the acid is the greatest when the acid in the solution amounts to somewhat more than* 1 *equivalent to* 1 *equivalent of ferric oxide.* When the acid is in larger quantity the amount of ferric oxide combined with 1 equivalent of acid is, as was to be expected, smaller. (With indefinitely much acid it would be indefinitely little.) The same relation, however, enters with smaller quantities of acid, where, on the contrary, one would *à priori* suppose that, an excess of ferric oxide being present, the acid would in greater measure be saturated with it.

Similar results are obtained with solutions of ferric nitrate containing different proportions of nitric acid. Thus, according to the preceding experiments:—

Iron in 100 cub. centims.	fe : N_2O_5.	x.	y.
0·479	100 : 73	31·9	0·93
0·266	103	18·8	0·79
0·185	132	8·2	0·69
0·139	164	6·7	0·57
0·111	197	5·6	0·48

In a solution containing about equal numbers of equivalents of ferric oxide and nitric acid, therefore, about 19 per cent. of the total amount of iron in the solution is present in the uncombined state, together with free acid; and the percentage falls, on the addition of 1 eq. more of nitric acid, to from 5 to 6 per cent. With these solutions a diminution of the value y with less content of acid does not appear to enter; to decide this point, however, further observations shall be instituted.

It is evident that, if the alteration of the magnetism with the temperature be determined for a solution of colloid ferric

oxide, as well as for a very acid solution of ferric chloride, the increase of dissociation with a rising temperature can also be directly determined by observation of the magnetism of neutral and other iron-solutions at different temperatures. But these experiments, like all the other magnetic observations on dissociation, present the difficulty that very precise observations are needed in order to obtain accurate results, since small errors in the determination of the magnetism have a great effect. On this, too, I reserve to myself a further communication.

If with the solution of a ferric salt that of another salt, of a different acid, be mixed, a partial exchange of the constituents of the two salts takes place. If the dissociation undergone by the newly formed iron-salt in the solution be different from that of the first employed, we can, from the alteration of the magnetism belonging to the unit weight of iron in the solution, first calculate the quantity of ferric oxide newly dissociated. In this way solutions of various sulphates were mixed with a solution of ferric chloride, which with not too great a dilution is scarcely dissociated. In the accompanying Table, under m is given the magnetism of the unit weight of iron in the mixture in percentages of that of the iron in non-dissociated iron-salts, under x the percentage amount of the dissociated ferric oxide:—

1 eq. ferric chloride with	eq.	m.	x.
Sulphate of soda.....	$\frac{1}{2}$	89·3	13·7
,, ,, ...	1	82·9	21·9
,, ,, ...	2	78·7	27·3
Sulphate of magnesia.....	$\frac{1}{2}$	91·6	10·8
,, ,, ...	1	85·8	18·2
,, ,, ...	2	83·7	20·9
Zincic sulphate	$\frac{1}{2}$	88·3	15·0
,, ,, ...	1	85·3	18·8
,, ,, ...	2	81·4	23·8
Cupric sulphate	$\frac{1}{2}$	93·4	8·5
,, ,, ...	1	89·2	13·8
,, ,, ...	2	84·7	19·6
Cobaltous sulphate	$\frac{1}{2}$	95·6	5·6
,, ,, ...	1	88·0	15·4
Nickelous sulphate	$\frac{1}{2}$	92·1	5·0
,, ,, ...	1	86·8	16·9

If we might assume that the ferric chloride which is not converted into ferric sulphate, even after the mixing is still contained undecomposed in the solution now poorer in ferric chloride, and that the ferric sulphate formed has, to the amount

of 25 per cent., been dissociated, the quantity of the latter formed would be obtained directly from the value x. These assumptions, however, are not strictly correct; and, moreover, the acid and base resulting from the dissociation might act further upon the other constituents of the solution, and consequently a change in the combining-proportions might ensue.

Leipzig, October 1876.

XXXVIII. *On the Nebular Hypothesis.*—VI. *Momentum and* Vis viva. *By* Pliny Earle Chase, *LL.D., S.P.A.S., Professor of Philosophy in Haverford College.*

[Continued from vol. iii. p. 211.]

IT is often more difficult to grasp truths which are presented under new aspects than those which are clothed in familiar garbs. It may therefore be well to glance at some of the most obvious tendencies to nodal action which result from simple gravitating fall towards a centre. The examination will be the more interesting and suggestive, because like tendencies must exist in all central forces which vary inversely as the square of the distance.

Ennis* has called attention to the fact that the difference between the velocity of infinite radial fall ($\sqrt{2gr}$) and circular-orbital velocity ($\sqrt{gr}$) must be accounted for in some way; and he thinks that it may be sufficient to explain all the phenomena of planetary rotation and revolution. In nebular condensation from r to $\frac{r}{n}$ the increase of radial velocity is $(\sqrt{n}-1)\sqrt{2gr}$; the circular-orbital velocity at $\frac{r}{n}$ is $\sqrt{ngr}$; therefore the increment of radial velocity would be sufficient to produce orbital velocity, in the periphery of an originally stationary nebula, when $(\sqrt{n}-1)\sqrt{2}=\sqrt{n}$; and

$$\therefore\ n=\frac{2}{3-2\sqrt{2}}=11{\cdot}65684.$$

If r be made to represent successively all points between secular aphelion and secular perihelion in the hypothetical nebulous belts which were condensed into Neptune, Uranus, Saturn, and Jupiter, this fall of condensation from Neptune would give orbital velocities in the Asteroidal belt; from Uranus, in the Mars belt; from Saturn, in the Venus belt; and from Jupiter, in the Mercury belt. Earth, as I have already shown, is at the centre of the primitive inter-asteroidal

* Phil. Mag. April 1877, pp. 262 *sqq.*

belt, which appears to have been thus broken up by the action of Uranus, Saturn, and Jupiter. By estimating the condensation from Neptune's mean distance, and from secular limits of Uranus, Saturn, and Jupiter, we find the following accordances:—

Neptune ...	$\div n = 2{\cdot}577$	Astræa	$= 2{\cdot}577$
Uranus s. p.*	$\div n = 1{\cdot}517$	Mars	$= 1{\cdot}524$
Saturn s. p.	$\div n = {\cdot}749$	Venus a.* ...	$= {\cdot}749$
Jupiter s. a.	$\div n = {\cdot}473$	Mercury s. a.	$= {\cdot}477$

This leaves the orbital velocities of the four outer planets to be accounted for by like condensation from an earlier nebulous condition of which we have no present visible evidence; but if the main hypothesis is correct, we may reasonably look for confirmation of a different kind within the present limits of the solar system. If we consider the *vis viva* of orbital and of radial velocity for unit of mass, the *vis viva* added by radial fall from r to $\frac{r}{m}$ is $(m-1)gr$, while the *vis viva* added by equivalent orbital contraction is only $\frac{1}{2}(m-1)gr$, or one half of the radial addition. A simple nebular condensation from r to $\frac{r}{2}$ would therefore add gr to the *vis viva*, which is equivalent to the *vis viva* of circular-orbital revolution at $\frac{r}{2}$. There is therefore a tendency to repeated nebular rupture at $\frac{r}{2}, \frac{r}{4}, \frac{r}{8}, \ldots \frac{r}{2^n}$.

Starting from the present outer limit of our system, Neptune's secular aphelion, these rupturing-nodes would occur at 15·235, 7·617, 3·809, 1·904, ·952, ·476, ·238! The first belt would include Neptune and Uranus; the second, Saturn; the third, Jupiter; the fourth, the Asteroids; the fifth, Mars and Earth; the sixth, Venus (grazing also the Earth and Mercury belts); the seventh, Mercury.

After the nebula had assumed a globular form, these rupturing nodes would occasion constant tendencies, from opposite extremities of every diameter, to the formation of confocal elliptic orbits, with major axes of $\frac{3r}{2}$ and minor axes of $\sqrt{8}r$. Those ellipses would mutually intersect at $\frac{2r}{3}$, thus tending, through collision of particles, to form a belt at that distance from the centre. The *vis viva* communicated by simple fall from r to $\frac{2r}{3} = \frac{1}{2}gr$, which is equivalent to *vis viva* of circular-

* a., mean aphelion; s. a., secular aphelion; s. p., secular perihelion.

orbital revolution at r, and also to the orbital *vis viva* gained by contraction from r to $\frac{r}{2}$. The internal motions and collisions of the particles of the belt would favour a condensation of the densest and comparatively inelastic materials, until the whole had acquired the mean orbital *vis viva*, $\frac{gr+2gr}{4}=\frac{3gr}{4}$, which is the normal orbital *vis viva* at the nodes of aggregating collision, $\frac{2r}{3}$. The following Table exhibits the double tendency, to nebular rupture and to nebular aggregation, starting from the point which would account for the orbital velocity of Neptune. The approximation of "B" to the planetary distance which would satisfy Bode's law, and the indications of Neptunian aggregation during direct fall towards the centre, lend new confirmation to the views which I have already expressed in regard to the *rationale* of Bode's law and the relative masses of the two outer planets:—

Rupturing-nodes.	Secondary nodes.	Planets.
$2\times$ ♆ s. a. 60·939	40·626	"B" =38·8
♆ s. a. 30·470	20·313	♁ s. a. =20·68
$\frac{1}{2}$ „ „ 15·235	10·157	♄ s. a. =10·34
$\frac{1}{4}$ „ „ 7·617	5·078	♃ s. p. = 4·89

The following Tables exhibit some of the modifying influences of other simple nodes:—

$\frac{2}{3}$♂	1·016	⊕	1·000	$\frac{1}{2}$♂	·762	♀ s. a.	·774
$\frac{2}{3}$⊕	·667	♀ s. p.	·672	$\frac{2}{3}\times\frac{2}{3}$♂	·677	♀ s. p.	·672
$\frac{2}{3}$♀	·482	☿ s. a.	·477	$\frac{1}{3}$⊕ s. p.	·466	☿ s. a.	·477
$\frac{2}{3}$☿ s. a.	·318	☿ s. p.	·297	$\frac{1}{3}$⊕ s. p.	·311	☿ s. p.	·297

In the intra-asteroidal belt and ellipse, which are bounded by ♂ sec. aph. and ☿ sec. per., we find

Middle of belt	1·017	Earth	1·000
„ ellipse ...	·719	Venus	·723.

Jupiter is similarly situated in reference to the Neptune-Uranian and the Uranus-Saturnian ellipses:—

Middle of ♆ s. a. ♁ s. a.	4·895	Middle of ♁ ♄	4·822	♄ s. p.	4·886
„ ♆ s. p. ♁	5·207	„ ♀ ♄ s. p.	5·225	♄	5·203
„ ♆ s. a. ♁	5·643	„ ♁ s. a. ♄	5·570	♄ s. a.	5·519

Saturn is similarly situated in reference to the Neptune-Saturnian and Sun-Uranian ellipses:—

Mid. ⊙ ♁ s. p.	8·844			♄ s. p.	8·734
„ ⊙ ♁	9·592	Mid. ♄ s. a. ♆ s. p.	9·628	♄	9·539
„ ⊙ ♁ s. a.	10·340	„ ♄ s. p. ♆ s. p.	10·432	♄ s. a.	10·343

There are doubtless many other results of early interorbital action, especially in connexion with collisions in confocal ellipses, which would furnish interesting subjects of investigation. For example, when the Jupiter belt was completely severed (♃ sec. per.), and the Earth and Venus belts were beginning to form (sec. aph.), the elliptic orbital collisions were near the limits of the Mars belt:—

Ell. coll.	♃ s. p. ⊕ s. a. 1·753	♂ s. a. 1·736
,,	♃ s. p. ♀ s. a. 1·337	♂ s. p. 1·311

If we take the radius of nebular rupturing-fall for the surface of Sun's homogeneous luminiferous atmosphere (2 × light-modulus), and reduce it in the ratio of mean radially varying to uniform circular velocity $\left(\frac{2}{\pi}\right)^*$, rupturing-nodes ($\frac{1}{2}$) and falls of condensation ($1 \div 11{\cdot}656854$) give the following Table:—

		1st c. fall.	2nd c. fall.	R. vec.	3rd c. fall.	R. vec.
$2\,M \div \left(\frac{2}{\pi} \times 11{\cdot}6569\right) =$		240·84	20·67	☉ s. a. 20·68	1·77	♂ s. a. 1·74
$M \div$	,,	120·42	10·33	♄ s. a. 10·34	·89	⊕ . p. ·93
$\frac{1}{2^5} M \div$	,,	60·21	5·17	♃ 5·20	·44	☿ s. a. ·48
$\frac{1}{2^4} M \div$	,,	30·10†	2·59	Ast. 2·59		
$\frac{1}{2^3} M \div$	,,	15·05	1·29	♂ s. p. 1·31		
$\frac{1}{2^6} M \div$	,,	7·53	·65	♀ s. p. ·67		

This seems to point, like the Neptune-Saturnian ellipse in a previous comparison, and like the present comparatively nebulous condition of Saturn itself, to Saturn as an important centre of early ring-aggregation, as if our nebula were at first a ring-vortex. The indication is confirmed by the similar densities of Saturn and Neptune, the similar densities of Uranus, Jupiter, and Sun, the fact that "these four planets form a system by themselves which is practically independent of the other planets of the system"‡, and the present approximate accordance between the transit of light through the Uranus-Telluric major axis and the time of planetary revolution at Sun's surface.

The peculiar indication of the Uranus-Telluric belt, the central position of Earth in the belt of greatest density, and the

* If synchronous undulations are intercepted by an obstacle, so as to produce accelerated motion towards a centre, the mean radius of variable motion is $\frac{2}{\pi}$ of the radius of corresponding uniform motion.

† ♆ = 30·03. ‡ Stockwell, 'Smiths. Contr.' 232. xiii.

absence of any explicit indications of our planet in most of the foregoing comparisons suggest the possibility that its place may have been fixed by a special law. Its secular perihelion (·932) is near the fifth rupturing-node of Neptune ($30{\cdot}034 \div 2^5 = {\cdot}939$).

The stellar-solar parabola* points to a time when α Centauri may have been at a nebular rupturing-point relatively to the Sun. The extreme estimates for $\frac{2}{\pi}\,\alpha$ Centauri are 28905200 and 30895100 solar radii. The seventh fall of condensation $(1 \div 11{\cdot}656854)^7$ would give ·988 and 1·056, showing a closeness of approximation to the present solar radius which can hardly be thought accidental. As there are two condensation-falls between $\frac{2}{\pi}$ Earth and Sun, there are five falls between α Centauri and Earth, the extreme estimates for α Centauri $\div 11{\cdot}656854^5$ being ·982 and 1·049 times Earth's radius vector. Both of these points are within the Earth belt (sec. per. = ·932, sec. aph. = 1·068).

Neptune's secular eccentricity seems to have been determined by the combined influence of condensation-fall, orbital collision, and rupturing-nodes; for Neptune's secular perihelion $\div 11{\cdot}656854 = 2{\cdot}53912$, $\frac{2}{\pi}$ sec. aph. $\div 2^3 = 2{\cdot}53913$.

The *Gegenschein*, and other indications that the zodiacal light may come from the remains of an early terrestrial ring, may lead us to look for evidences of residuary nebular activity in some of the outer planets. A radial oscillation at Uranus's secular aphelion would be accomplished in $10{\cdot}3396^{\frac{3}{2}} = 33{\cdot}247$ years, a circular revolution at Saturn's sec. aph. in $10{\cdot}3433^{\frac{3}{2}} = 33{\cdot}265$ years, a circular revolution at Jupiter's mean perihelion in $4{\cdot}9782^{\frac{3}{2}} = 11{\cdot}108$ years. The November meteoric cycle is 33·25 years; the Wolf sun-spot cycle 11·07 years.

There is a noteworthy numerical correspondence between the seven rupturing-nodes within the planetary belt and the seven condensation-falls from α Centauri to $\frac{\pi}{2}$ Sun. The fifth node and the fifth fall both come within the Earth belt.

If we suppose seven successive transformations of uniform into variable velocity before the determination of the present solar mass and light-modulus, and five condensation-falls ($n = 11{\cdot}656854$) after each transformation, we find the following approximations:—

* IV. π, Phil. Mag. Sept. 1876.

$\pi^7 \mathrm{M} \div n^5 =$	30·941	♆ sec. aph.	30·470
$\pi^6 \mathrm{M} \div$,,	9·849	♄	9·548
$\pi^5 \mathrm{M} \div$,,	3·135	Hygeia.	3·121
$\pi^4 \mathrm{M} \div$,,	·998*	⊕	1·000
$\pi^3 \mathrm{M} \div$,,	·318	☿ sec. per.	·297
$\pi^2 \mathrm{M} \div$,,	·101		
$\pi \mathrm{M} \div$,,	·032		

The probability of undulatory gravitating action is increased by the investigations of Bjerknes, who has shown (*Comptes Rendus*, lxxxiv. p. 1377) that two spheres having concordant pulsations attract each other inversely as the square of the distance, and that they repel each other according to the same law if their pulsations are opposed.

The use of the parabola † in representing expanding action is recognized by H. Sainte-Claire Deville, who states, in considering cases where the vapour-densities vary with the temperature (*Comptes Rendus*, lxxxiv. p. 1257), that "the movement of a material point may be accurately enough represented by a parabolic function of the second degree already employed by M. Fizeau." Deville hopes to employ the resulting relations usefully in expounding some principles of Thermochemistry.

The hypothesis that the radial *vis viva* of mean rectilineal velocity may be taken as the representation of increments of heat under constant volume, while the radial *vis viva* of synchronous constant velocity will represent simultaneous increments of heat under constant pressure ‡, assumes that the gaseous condition is perfect. W. M. Hicks (Phil. Mag. June 1877) says:—"If, then, the two atoms of a molecule become separated, there seem only two ways of accounting for it: either their relative motion becomes so large as to overcome the force of attraction; or some external force must act upon them, which can be nothing else than a reaction between them and some other molecule. The latter is the hypothesis I have adopted in the following investigation." Under this hypothesis, by taking the potential energy of combination of a single molecule at its upper limit and with special temperature-conditions, he obtains $\frac{c'}{c} = 1{\cdot}423$; my own ratio, deduced from his former hypothesis (see Phil. Mag. Sept. 1876, γ, δ) being $\frac{c'}{c} = 2\pi^2 \div (\pi^2 + 4) = 1{\cdot}4232$. If this coincidence is merely accidental, it is very curious. It seems, as I think, to justify

* $\pi^4 \mathrm{M} =$ distance of α Centauri. † Proc. S. Phil. Amer. xvi. p. 507.
‡ Ibid. xiv. p. 651.

both my own view of the kinetic energies of perfect gases, and Hicks's view of the importance of temperature-relations in condensable gases.

The variation of the nucleal radius as the $\frac{3}{4}$ power of the atmospheric radius (Phil. Mag. Sept. 1876, κ) may furnish a mechanical explanation of results which seem to have been obtained independently, and nearly simultaneously, by Silas W. Holman (Phil. Mag. Feb. 1877) and E. Warburg (Pogg. *Ann.* clix. p. 415). Holman concludes, from the results of a number of careful experiments, that the "viscosity of air increases proportionally to the 0·77 power nearly of the absolute temperature between 0° and 100° C." The extreme range of his results is ·738 to ·799. Warburg, from experiments both with hydrogen and with air, deduces the exponents between 20° and 100°, ·76 for air (the extremes being ·74 and ·76), and "about $\frac{2}{3}$" for hydrogen (the extremes being ·57 and ·65). The closeness, the narrow range, and the mutual confirmation of these independent results, as well as the new analogy between molar and molecular forces which seems to be indicated by the atmospheric experiments, are all interesting. The viscous particles, so far as they are affected by the same movements, may be compared to the rotating particles of a solid nucleus; the thermal undulations, in a supposed æthereal medium, present a like analogy to the motions of an elastic atmosphere. The well-known anomalies in the elasticity of hydrogen are in accordance with its low viscosity. Warburg's extremes (hydrogen ·57, air ·76) seem to indicate secondary nucleal and atmospheric relations between air and hydrogen.

In my identification of the velocity of solar dissociation with the velocity of light (Phil. Mag. *l. c.*, ζ to ι inclusive), although the conception of successive wave-impulses seems most natural, it is by no means essential; if the pressure of the ultimate force is constant, the result is the same. The ratio of the velocity of dissociation to the velocity of perfect fluidity (ib., η, θ) is approximately illustrated by Draper's estimate of the ratio between the temperature of glow (977° F., or 1436° from absolute 0°), and the temperature of fluidity (32° F., or 491° from absolute 0°), $1436 \div 491 = 2{\cdot}9$. Here complete fluidity is compared with incipient glow. The ratio $\pi : 1$ would require an additional allowance of 107°, or about 7·5 per cent. for the difference between the temperatures of complete and incipient glow, and for other considerations.

The *vis viva* of terrestrial dissociation being equivalent to half the *vis viva* of incipient planetary dissociation at the sun (ib., λ, μ, ν), the temperature-ratio of water-vaporization to

dissociation furnishes another illustration of a similar character. Deville (*Comptes Rendus*, lxxxiv. p. 1259) says:—"My first experiments on the dissociation of water, in perfect accord with those which M. Bunsen has since published, demonstrate that at temperatures of 2500°, according to M. Debray and myself, or of 2800°, according to the illustrious professor of Heidelberg, nearly half of this vapour is reduced to its elements, hydrogen and oxygen." The ratio 2800° : 100° agrees precisely with a very probable estimate of the ratio between solar and terrestrial superficial attraction.

XXXIX. *On the Seismic Results obtained from the Hallet's-Point Explosion.*

To the Editors of the Philosophical Magazine and Journal.

Gentlemen,

WILL you allow me space for a few observations upon some of the results of the great explosion of Sept. 24, 1876, at Hallet's Point, New-York Harbour, as I find them recorded in a printed copy of a paper read before the National Academy of Sciences of America, Oct. 18, 1876, and before the Essayons Club of the Corps of Engineers, Nov. 14, 1876 (vol. xl. of printed papers). For a copy of this paper by Major-General Abbot, U.S. Engineers, I believe I have been indebted to that officer, who transmitted it through my son, Dr. J. W. Mallet, Professor of Chemistry, University of Virginia, some time since, though I have but recently been able to make myself acquainted with its contents. While the primary object of this great explosion was the engineering one of destroying the reef, which appears to have been most successfully accomplished, a subsidiary object of a purely scientific character was sought to be attained, viz. the determination of the transit-velocity, or rate of progression, of the elastic wave of shock through those superficial portions of the earth's crust adjacent to the seat of explosion. I cannot but regret that this experiment was ever attempted, as the circumstances of the case are so ill suited to the determination of so delicate a physical question as, in my judgment, to be rather calculated to retard than advance our knowledge of observational seismology. I shall not presume to occupy your space by recurring to the details of the arrangements of the explosion, but refer such of your readers as take an interest in the subject to Major-General Abbot's paper, and proceed at once to remark:—

It is of primary importance to any accurate determination of

the velocity of seismic-wave transit that the instant of genesis of the wave, or instant at which during the period of genesis the wave whose transit-velocity is to be measured starts, should be accurately known ; and for this the impulse generating the wave must result from one single explosion ; and, if possible, the commencement of movement of the rock-mass should be visible from the distant time-observing-point at the extremity of the measured range. Now in this case the impulse was due, not to one explosion, but to thousands of small charges scattered in various directions within a limited but considerable distance from each other, and supposed to be galvanically fired all at the same instant, as no doubt they were, so far as skilful arrangements could permit ; but however apparently simultaneous as judged by the senses, the impulse generated by such a rapid crackle of small explosions is very different from that produced by a single mass of an explosive agent, or even by three or four such large masses exploded very near each other. I conceive it therefore impossible with sufficient exactitude to assign the instant at which the wave of shock started in this instance ; and to assume the appearance of disturbed water above the seat of explosion, or the shock felt from the ground closely adjacent to it as marking that instant, seems to me, in either choice, to neglect many sources of error.

The transit-rate was observed at four points, at different distances and situated at various azimuths and under very different surface conditions, along the shores of the bay and of the river Hudson. As to the results of observation made at each of these four stations, viz. (1) Fresh-Pond Junction, (2) Willet's Point, (3) Jamaica, (4) Springfield Junction, situated at the respective distances of 5·134, 8·33, 9·333, 12·769 miles from the explosion, it is startling to find that there is not even a near approximation to agreement between them, and that the transit-velocity given by No. 2 (8300 ft.) is more than double that given by No. 1 (3873 ft.), and nearly double that given by No. 3 (4521 ft.), while No. 4 (5309 ft.) presents a velocity which, though intermediate between these widely sundered extremes, presents no semblance of agreement with any of the three other results. Of the two experiments which present some semblance of approach to agreement, No 1 (3873 ft.) and No. 3 (4521 ft.), I find the first marked as questionable (?) ; and if this be thrown out, there remains not even a semblance of agreement between the other three results. I am therefore compelled to look with entire distrust upon all these results. In every case the wave-transit occurred through earth covered for very variable portions of the entire range by water variously in motion,

and differing much in depth at various parts. Now, as seismic wave-transit is much more rapid through water than through any known rock or other formation, and as the impulse was transmitted from about the same focus through the water and the earth it partially or wholly covered, it is exceedingly improbable that the rapid rate of transit in the water should not more or less influence that through the rock beneath. There then must arise, as it seems to me, great difficulty in knowing what wave it was that the observers at the different extremities of the different ranges noticed by their instruments. It is certain that no two of the observers could have seen the same wave under like modifications, due to the unlike circumstances of transmission in the different respective ranges.

Nor, amongst the numerous sources of uncertainty present, must we omit to notice that there were at least three sets of waves generated at the outset, viz. (1) that of the crackling explosion itself, (2) that of the fall of the dislocated masses of rock into the cavity excavated beneath the reef, (3) the return fall of the huge mass of water thrown up by the explosion. The further an elastic vibration travels through any part of our earth's crust, the more it gets broken up and diffused as secondary waves; hence very long ranges are less suited for experiment than those of more moderate length, and moderate charges are on the whole better than very powerful ones. From all these causes, therefore, it seems impossible to decide what was the true origin of the "tremor" seen in the seismoscope by each respective observer. The tremor at each station is stated to have lasted for several seconds; but I do not find it stated whether the time of arrival is noted from the commencement, middle, or end of this period.

Nothing is mentioned in the paper referred to as to the nature of the rock or other formations through which the transit-ranges lay. From other sources of information, however, I presume they were all in more or less stratified and disturbed rock, that the line of each range was through different and partially overlying strata. Now my own experiments made in the neighbourhood of Holyhead, North Wales (Phil.Trans.1861–62), have proved the very considerable differences in transit-velocity in the same rock in the direction of the strata and transverse to the same; so that from this cause alone it appears to me that the transit-velocity through none of the ranges here referred to could be truly comparable, even if the true transit-rate through any one of them were actually attainable.

The distances of the various observing-stations from the focus of explosion are stated to have been measured off from

certain railway maps and those of U.S. Coasts Survey. I know not what amount of precision belongs to the Coasts Survey of New-York Harbour and the Hudson River. I readily credit it with all the exactitude which characterizes the national scientific work of the United States; but I cannot credit any Coasts Survey designed for maritime commercial and social purposes, extending, as in this case, over an extreme range of several miles of coast, as assuring sufficient exactness to be made the basis for the measurement of distance as an element for determining any great physical problem. Nor do the instrumental arrangements for noting the time of arrival of the several waves at the several stations seem to me wholly free from objection. A more exacting critic than I am at all disposed to be, must remark that, amongst the four different observers, no attempt seems to have been made to determine the personal equation of any one of them; the differences due to the different observers would very differently perplex the results where their respective ranges differed so much in length as well as in other conditions, and where in each case three senses (hearing, seeing, and nerve-transmission) were brought into play.

From all these circumstances, as well as from others which for brevity I omit to notice, I cannot regard the results obtained by these operations as of authority; and I feel justified in protesting against their being viewed as any scientific check or control, or as capable of revising the results obtained by myself several years ago upon simpler and more ascertainable data and by more exact methods, in part with the assistance of my eldest son, Dr. J. W. Mallet. As my son is intimately acquainted with the conditions involved in seismologic investigation and with the methods and precautions adopted by me, I cannot but presume that he was not fully informed as to the circumstances relating to this great explosion in New-York Harbour when he suggested its subsidiary application to seismic physics, which I learn he did from the first paragraph in General Abbot's paper, by a communication addressed to the Smithsonian Institute in June 1876.

In these objections I wish to be clearly understood as having no *à priori* difficulty in accepting a higher velocity of wave-transit than the highest attained experimentally by myself. It is highly probable that such may be elicited by future experiment. But should such cases arise, their results, like all great physical truths, should only be credited upon unexceptionable observations or experimental evidence. While feeling justified in making these objections, I wish to disclaim all controversial spirit or intention; loss of sight, indeed, and dimi-

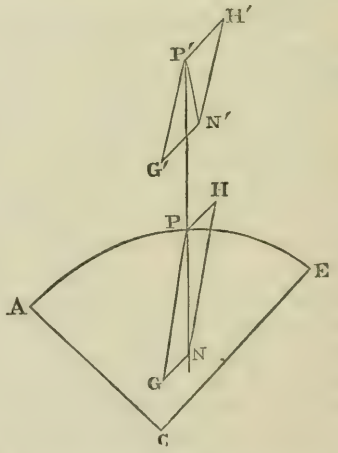
nished energy would prevent my engaging in any scientific controversy, were any called for.

ROBERT MALLET.

London, September 17, 1877.

XL. *On a Correction to Observed Latitudes.* *By* Colonel A. R. CLARKE, *C.B., F.R.S.*

I do not know that any demonstration has ever been given of a theorem enunciated by Gauss in a letter addressed by him in 1853 to General Baeyer. It appears from the letter in question (of which a translation appeared in the *Comptes Rendus des Séances de la Commission permanente de l'Association Géodésique internationale tenues à Florence en* 1869) that, at the suggestion of General Baeyer, Gauss had investigated the influence of altitude above the sea-level on observed latitudes, and had arrived at a result which, if not very important to geodesists and astronomers, still is very curious and interesting. The point in question is this:—In the adjoining diagram let A P E be a quadrant of a meridional section of the earth, N P P′ the normal at any point P. Let P N represent gravity at P; and on the same scale let P H, parallel to the equator C E, represent the centrifugal force at the same point; then completing the parallelogram G H, P G will be the attraction of the earth. At a point P′ vertically above P the centrifugal force P H is increased to P′ H′, retaining its parallelism; and the attraction P G is diminished to P′ G′—not, however, parallel to its former direction, for G P G′ P′ converge towards the zenith. The resultant gravity P′ N′ at P′ is therefore no longer of necessity in the line P′ P; and the point to be determined is the magnitude of the angle P P′ N′.



The potential of the spheroid $(x^2+y^2)(1-2\epsilon)+z^2=c^2$, whose

* Communicated by the Author.

semiaxes are c and $c(1+\epsilon)$, ϵ being a very small quantity whose square may be neglected, at an external point whose coordinates are f, 0, h, is

$$V=\frac{M}{r}\left\{1+\frac{\epsilon c^2}{5r^4}(f^2-2h^2)\right\},$$

where M is the mass of the spheroid ; if ρ be the density,

$$M=\tfrac{4}{3}\pi\rho c^3(1+2\epsilon).$$

If the spheroid, instead of having a uniform density ρ, be formed of homogeneous spheroidal shells having a common centre and axis of rotation, the ellipticity as well as the density of these shells varying from the centre to the outer surface, and so being a function of the variable polar semiaxes c', then it is easy to see that the potential of such a heterogeneous spheroid is

$$V=\frac{4\pi}{3}\cdot\frac{\phi(c)}{r}+\frac{4\pi}{15}\psi(c)\frac{f^2-2h^2}{r^5},$$

where c is the polar semiaxis of the outer surface, and

$$\phi(c)=\int_0^c\rho\frac{d.c'^3(1+2\epsilon)}{dc'}dc' : \psi(c)=\int_0^c\rho\frac{d(c'^5.\epsilon)}{dc'}dc'.$$

In the theory of the figure of the earth it is shown that the condition of fluid-equilibrium implies the relation

$$\left(\epsilon-\frac{m}{2}\right)c^2\phi(c)-\tfrac{2}{5}\psi(c)=0,$$

ϵ being the ellipticity of the external surface, and m the ratio of the centrifugal force at the equator to the attraction of the earth there. The value of m is, neglecting small quantities of the second order, given by the equation

$$\frac{4\pi m}{3}\cdot\frac{\phi(c)}{c^3}=\omega^2,$$

where ω is the angular velocity of the earth. Now, since $M=\frac{4}{3}\pi\phi(c)$, we get for V the form

$$V=\frac{M}{r}+\frac{M}{3}c^2\left(\epsilon-\frac{m}{2}\right)\frac{f^2-2h^2}{r^5}.$$

This value of the potential is arrived at on the hypothesis of a certain distribution of matter in the interior of the earth ; but it is important to remark that it has been obtained by Prof. Stokes (Cambridge and Dublin Mathematical Journal, vol. iv. p. 207) without any such hypothesis as to the distribution of density, be the interior fluid or solid, but assuming only that the surface is a spheroid of equilibrium of small ellipticity.

Now let X, Z be the components of the attraction of the earth at P parallel respectively to the equator and to the polar axis, F the centrifugal force at P; then, ϕ being the latitude of P, we have the necessary relation $(X-F)\tan\phi=Z$. At P′, instead of X−F and Z, we have $X-F+\delta(X-F)$ and $Z+\delta Z$; and these will correspond, not to $\tan\phi$ but to $\tan(\phi+\delta\phi)$. Hence, differentiating, we have

$$(\delta X-\delta F)\sin\phi-\delta Z\cos\phi=-Z\operatorname{cosec}\phi\delta\phi.$$

Now $X=-\frac{dV}{df}$, and $Z=-\frac{dV}{dh}$; and if we put n for the height P P′, we have in passing from P to P′,

$$\delta f=n\cos\phi,\quad \delta h=n\sin\phi,$$

and

$$-\delta X=n\cos\phi\frac{d^2V}{df^2}+n\sin\phi\frac{d^2V}{df\,dh},$$

$$-\delta Z=n\cos\phi\frac{d^2V}{df\,dh}+n\sin\phi\frac{d^2V}{dh^2},$$

whence

$$\frac{Z}{n\sin\phi}\delta\phi=\sin\phi\cos\phi\left(\frac{d^2V}{df^2}-\frac{d^2V}{dh^2}\right)+\frac{d^2V}{df\,dh}(\sin^2\phi-\cos^2\phi)+\omega^2\sin\phi\cos\phi.$$

The values of the differential coefficients are found to give

$$\frac{d^2V}{df^2}-\frac{d^2V}{dh^2}=3M\frac{f^2-h^2}{r^5}+Mc^2\left(\epsilon-\frac{m}{2}\right)\frac{7f^4+12h^4-51f^2h^2}{r^4},$$

$$\frac{d^2V}{df\,dh}=3M\frac{fh}{r^5}+Mc^2\left(\epsilon-\frac{m}{2}\right)\frac{15f^2-20h^2}{r^9}fh,$$

where $r^2=f^2+h^2$. Also

$$\sin\phi=\frac{h}{r}\left(1+2\epsilon\frac{f^2}{r^2}\right),$$

$$\cos\phi=\frac{f}{r}\left(1-2\epsilon\frac{h^2}{r^2}\right).$$

Substituting these in the expression for $\delta\phi$, the result after some little reduction is

$$\frac{Z}{\sin\phi}\delta\phi=n\frac{M}{c^5}fh\left(6\epsilon-8\left(\epsilon-\frac{m}{2}\right)+m\right).$$

Now, with sufficient approximation,

$$\frac{Z}{\sin\phi} = \frac{M}{c^2},$$

$$\therefore \delta\phi = \frac{n}{c}(5m-2\epsilon)\frac{fc}{c^2}$$

$$= \frac{n}{c}\left(\frac{5}{2}m-\epsilon\right)\sin 2\phi\ ;$$

or, if g' and g be the values of gravity at the pole and at the equator respectively, then, making use of Clairaut's theorem,

$$\delta\phi = \frac{n}{c}\cdot\frac{g'-g}{g}\sin 2\phi.$$

This result is certainly remarkable for its simplicity; but, practically, for ordinary mountain-heights it only amounts to a small fraction of a second.

XLI. *Notices respecting New Books.*

An Elementary Treatise on the Dynamics of a System of Rigid Bodies. With Numerous Examples. By Edward John Routh, *M.A., F.R.S., F.R.A.S., F.C.S., &c., late Fellow and late Assistant Tutor of St. Peter's College, Cambridge; late Examiner in the University of London. Third Edition, Revised and Enlarged.* London: Macmillan and Co. 1877. (8vo, pp. 564.)

MR. ROUTH'S Treatise on Rigid Dynamics has been for several years the Text Book commonly used by students who "take up" that branch of mechanical science; so that it may be presumed that those who have paid any attention to the subject, are more or less acquainted with one or other of the earlier editions. The present edition, the third, appears in a different form from those which preceded it, and has been very considerably enlarged. In fact, when both the size of the pages and their number are taken into account, we shall not be far wrong in stating that it is larger by one half than the second edition. So that it is a very large volume; and, further, it contains much more matter than the mere number of the pages might lead one to expect.

The work is designed to meet the wants of two classes of students—those who wish for information on the higher parts of Dynamics, and those "to whom the subject is entirely new." The parts to which the attention of the latter class should be directed are indicated by a selection of articles comprising about a third of the volume. The remaining two thirds contain most of the additions. The author's aim in making these additions has been to give the student at least some notion of the most important applications of the general doctrines of Dynamics to particular cases; so that, although such a subject as rigid dynamics might at first sight be thought to be contained within narrow limits, yet in reality the author has had to deal with an extensive literature of

memoirs, and has had to study compression in every possible way. In some cases the results of an extensive investigation are stated in a short article; in others important theorems are given in the form of examples, the reasoning by which their truth is established being left to be made out by the student with little or no assistance. Thus, on p. 139 Mr. Routh gives as an example M. Morin's experimental proof that impulsive friction obeys the laws of ordinary friction; in Art. 151 he gives (with certain variations), the substance of M. Morin's investigation of the friction of carriage-wheels; in Art. 224, under the head of an example he gives four of the principal theorems of Mr. Ball's Theory of Screws; and similar cases are to be found elsewhere—*e. g.* Ex. 2 p. 312, Ex. 1 p. 366, Ex. 1, 2 p. 371, Ex. 4 p. 498, &c. All these are, we believe, additions made to the present edition.

In other cases the additions are supplementary to articles that occurred in former editions. Thus, in Chap. IX. (on the motion of a body under the action of no forces), in this and in former editions, the determination of the angular velocities round the principal axes is shown to depend on a differential equation, the integration of which can be made without difficulty to depend on an elliptic Integral. In the present edition the solution is actually effected by means of elliptic functions, according to a method due to Kirchhoff.

In a case where the matter of a book is very closely packed, and where a good deal of detail is left to be made out by the reader, there is of course considerable danger of needful explanation being altogether withheld, or given with so much brevity as to be insufficient for the wants of many of the readers. Although Mr. Routh's explanations are for the most part sufficient, and in many cases singularly clear, yet we cannot help thinking that occasionally his text might be expanded with advantage. We will give an example of what we mean. On p. 411, in the chapter on the motion of a body under the action of no forces, after defining the polhode, and showing that its equations are

$$\left.\begin{aligned} A^2x^2+B^2y^2+C^2z^2&=\frac{MG^2\epsilon^4}{T},\\ Ax^2+By^2+Cz^2&=M\epsilon^4, \end{aligned}\right\}$$

our author goes on thus:—

"Eliminating y, we have

$$A\,(A-B)\,x^2+C\,(C-B)\,z^2=\left(\frac{G^2}{T}-B\right)M\epsilon^4.$$

"Hence if B be the axis of greatest or least moment of inertia, the signs of the coefficients of x^2 and z^2 will be the same, and the projection of the polhode will be an ellipse. But if B be the axis of mean moment of inertia, the projection is an hyperbola.

"A polhode is therefore a closed curve drawn round the axis of greatest or least moment, and the concavity is turned towards the axis of greatest or least moment, according as $G^2 \div T$ is greater or less than the mean moment of inertia."

Now, putting out of the question the curious clerical error—for such we suppose it to be—of calling B the axis of greatest or least moment of inertia, we cannot help thinking that if we were to write down all the steps needed to justify the conclusion, it would appear that most of them are suppressed, and that even if only the principal steps were indicated, still the paragraph would need considerable expansion. The above extract, it must be remembered, occurs in one of the articles designed for students to whom the subject is entirely new. We cannot help thinking that such a student might spend a long time over it, and have after all to get help from his private tutor before fairly making out its meaning.

The merits of Mr. Routh's Treatise are so great and so generally acknowledged, that we are sure the purpose of our remarks will not be misunderstood. It is merely this, that the above-quoted passage leaves too much to be made out by the unaided sagacity of a student who is just beginning a difficult part of a difficult subject. We suspect that a careful examination of the volume would reveal other points in which greater fulness of exposition would be of advantage to the student.

An Elementary Treatise on the Integral Calculus, containing Applications to Plain Curves and Surfaces; with Numerous Examples. By Benjamin Williamson, *M.A., Fellow and Tutor, Trinity College, Dublin. Second Edition, Revised and Enlarged.* London: Longmans, Green, and Co. 1877. (Crown 8vo, pp. 348.)

We gave a brief account of this work on the appearance of its first edition (vol. xlix. fourth series, p. 319), and what we then said of it is applicable to the present edition—except that we have to notice the addition of two chapters, which together increase the volume by more than a fourth part. The first of these chapters is on "Moments of Inertia." It contains not merely an account of the methods of determining the moments of Inertia of bodies with reference to given axes, but also enters into the determination of products of Inertia, and questions connected with the momental ellipsoid and principal axes of a solid. In fact, its contents coincide pretty closely with those of the chapter on moments of Inertia and principal axes, which usually forms part of a treatise on the motion of a rigid body. For the methods adopted in the chapter the author is "indebted to the kindness of Professor Townsend." There is, we conceive, a distinct advantage in making such a chapter part of an Elementary Treatise on the Integral Calculus; but we think the author might have gone further, and should have inserted a chapter on the determination of centres of gravity. These determinations, like those of moments of Inertia, form a branch of Geometry which it is a gain for the student to understand, and to have had practice in, before entering on the more advanced parts of Mechanics.

The second chapter peculiar to the present edition is on "Mean Value and Probability," and, of course, relates to those cases in which the magnitude to be considered is subject to continuous

change, and in which, therefore, the aid of the Integral Calculus is required. This chapter (which is written by Professor Crofton, of Woolwich) is devoted to the consideration of "a few of the less difficult questions on these subjects," and is intended "to give at least some idea of the methods to be employed." There is, of course, a certain order in the arrangement of the questions, but hardly what amounts to a systematic treatment of the subject; in fact the number and diversity of questions on probability is "so great that no attempt seems to have been made to classify or connect them into a regular theory" (p. 311). So that, in fact, the chapter consists of a number of explanatory articles of a more or less general character, each article being followed by a few examples fully worked out (in all about forty) of such a kind as might be anticipated—*e. g.* "To find the mean distances between two points within a given circle" (p. 304), or again, "Three points being taken at random within a sphere, to find the chance, that the triangle which they determine shall be acute-angled" (p. 327). It is needless to say that such questions are excellent exercises in the Integral Calculus, are likely to interest an intelligent student, and that the chapter containing them is a very useful and interesting addition to an admirable elementary treatise.

XLII. *Proceedings of Learned Societies.*

ROYAL SOCIETY.

[Continued from p. 234.]

March 22, 1877.—Dr. J. Dalton Hooker, C.B., President, in the Chair.

THE following paper was read:—

"On Friction between Surfaces moving at Low Speeds." By Fleeming Jenkin, F.R.SS. L. & E., Professor of Engineering in the University of Edinburgh, and J. A. Ewing.

The common belief regarding friction, which is based on the researches of Coulomb and Morin, is that between surfaces in motion the friction is independent of the velocity, but that the force required to start the sliding is (in some cases at least) greater than the force required to overcome friction during motion; in other words, the static coefficient is usually considered to be greater than the kinetic. It occurred to the authors that there might possibly be continuity between the two kinds of friction, instead of an abrupt change at the instant in which motion begins. We should thus expect that when the relative motion of the surfaces is very slow there will be a gradual increase of friction as the velocity diminishes. Whether any such increase takes place at very low speeds is left an open question by the experiments of Coulomb and Morin, whose methods did not enable definite measurements of the friction to be made when the velocity was exceedingly small. The authors have succeeded in measuring the friction between surfaces moving with as low a velocity as one five-thousandth of a foot per

second, and have found that in certain cases there is decided increase in the coefficient of friction as the velocity diminishes.

The apparatus made use of consisted of a cast-iron disk 2 feet in diameter and weighing 86·2 lbs., supported on a steel axle whose ends were less than one tenth of an inch in diameter. These ends were supported in bearings which consisted of rectangular notches cut in pieces of the material whose friction against steel was to be measured. The disk was caused to revolve and then left to itself, when it came to rest in consequence of the friction on the ends of the axle. The rate of retardation was found as follows:—A strip of paper $2\frac{1}{2}$ inches broad was stretched round the periphery of the disk; and a pendulum was caused to swing across this paper in a plane perpendicular to that of the disk. On the pendulum was fastened a fine glass siphon, one end of which dipped into a box containing ink, whilst the other stood at a short distance from the paper strip, across which it was carried as the pendulum oscillated. By keeping the ink-box strongly electrified, ink was deposited on the paper by the point of the siphon in a rapid succession of fine spots. By this means, without the introduction of any new source of friction, a permanent record was made of the resultant motion of the pendulum and the revolving disk. This frictionless method of recording was designed by Sir William Thomson for telegraphic purposes, and is employed in his siphon recorder. From the curve drawn in this way it was easy to determine the rate of retardation of the disk (and therefore the friction) corresponding to various velocities of the rubbing surfaces. The lowest velocity for which the determinations were definite was about 0·0002 foot per second; and the highest velocity to which the experiments extended was 0·01 foot per second. The surfaces examined were steel on steel, steel on brass, steel on agate, steel on beech, and steel on greenheart—in each case under the three conditions, dry, oiled, and wet with water. In the cases steel on beech oiled or wet with water, and steel on greenheart oiled or wet with water, the coefficient of friction increased as the velocity diminished between the two limits given above, the increase amounting to about twenty per cent. of the lower value. It appeared that at the higher limit of velocity there was little further tendency to change in the coefficient; but it is impossible to say how much additional change might take place between the lower limit of the velocity and rest. In the case of steel on agate wet with water there was a similar but much less marked increase of friction as the velocity decreased; and in the case of steel on steel oiled there was a slight and somewhat uncertain change of the opposite character—that is, a decrease of friction as the velocity decreased. This case, however, would require further examination. In all other cases the friction seemed to be perfectly constant and independent of the velocity. Out of all the sets of circumstances investigated, the only ones in which there was a large difference between the static and kinetic values of the coefficient of friction were those in which a decided increase was observed in the kinetic value as the speed

decreased. This result renders it exceedingly probable that there is continuity between the two kinds of friction.

GEOLOGICAL SOCIETY.

June 20th, 1877.—Prof. P. Martin Duncan, M.B., F.R.S., President, in the Chair.

[Continued from p. 237.]

10. "The Exploration of the Ossiferous Deposit at Windy Knoll, Castleton, Derbyshire, by Rooke Pennington, Esq., LL.B., F.G.S., and Prof. W. Boyd Dawkins." By Prof. W. Boyd Dawkins, M.A., F.R.S., F.G.S.

11. "Description of the Fossil Organic Remains from Bendigo." By M. Carl August Zachariæ.

12. "Notes on some recent Discoveries of Copper-ore in Nova Scotia." By Edwin Gilpin, Esq., M.A., F.G.S.

The author described the occurrence in the northern part of Nova Scotia of a great band of Silurian deposits, running nearly east and west, and traversed in a corresponding direction by numerous detached bands of granites, syenites, &c. Roughly parallel to the line of the latter there is a tolerably well-defined series of fractures running from Parrsboro on the Bay of Fundy to Guysboro on the Atlantic coast. The course of this line of disturbance is marked by metamorphism, and by the presence of associated ores of iron and copper. The principal localities where the latter occur are noticed by the author, who states that the copper deposits attain their greatest development near Lochaber Lake and Polson's Lake, where they form a series of veins cutting at oblique angles black and red shales and quartzites, apparently of somewhat doubtful age. The quality of the ore is said to be good.

13. "Glacial Drift in the North-eastern Carpathians." By R. L. Jack, Esq., F.G.S., and John Horne, Esq., F.G.S., of the Geological Survey of Scotland.

In this paper the authors noticed the statements of previous observers as to the occurrence of glacial drift in the northern part of the Carpathian range, and described the rock-formations surrounding the head-waters of the Theiss, and some drift sections observed in the valley of that river. They arrived at the following conclusions:—Glacial deposits are not abundantly developed in the valleys of the north-eastern Carpathian. The drift in the upper reaches of the Theiss is of the most fragmentary character, and is confined mainly to the broader portions of the valley. There is, however, sufficient evidence for maintaining that the Theiss valley was filled with a glacier upwards of 45 miles long, although the authors were unable to determine whether this glacier ever debouched on the plains of Hungary or ever reached the edge of the Carpathian chain; but they think it probable that such was the case.

14. "On Terminal Curvature in the South-western Counties." By W. A. E. Ussher, Esq., F.G.S., of H.M. Geological Survey.

The author discussed the views advocated by Mr. D. Mackintosh on the terminal curvature of slaty beds (Q. J. G. S. vol. xxiii. p. 326), and objected to the hypothesis that the phenomenon was produced by the action of ice in any form, which was the agency to which Mr. Mackintosh was most inclined to ascribe it. The author thought that what has been called terminal curvature might be produced by three distinct causes, namely:—1. The curvature produced by internal movements at great depths, afterwards rendered superficial by long subsequent denuding agencies; 2. The action of wedging frosts on the upturned edges of the beds, as advocated by Mr. Godwin-Austen; and 3. The intrusion between the laminæ of the rocks of the roots and rootlets of growing trees.

15. "On the Chronological Classification of the Granitic Rocks of Ireland." By G. H. Kinahan, Esq., M.R.I.A.

The author adopts Scheerer's definition that a *granite* is a rock of certain constitution, in which all the constituents are separately developed, and gives the name of *elvanites* to those granitic rocks in which part of the constituents are not perfectly crystallized. The elvanites pass into true granites on the one hand, and on the other into plutonic or volcanic rocks. They are thus "passage-rocks" between the two sections.

The author apparently regards all granites as formed by the metamorphosis either of the sedimentary rocks in which they occur, or of the plutonic rocks associated with these. Even intrusive granites are the product of an extreme degree of metamorphosis. Of metamorphosis he distinguishes two kinds, namely:—*Metapepsis*, or regional metamorphosis, extending over larger or smaller areas, and due to aqueo-igneous action; and *Paroptesis*, or local metamorphosis, caused by heat generated at or near local igneous action or a protrusion or sheet of igneous rock.

The author then indicates the application of these principles to the classification of the granitic rocks of Ireland in the chronological order of the sedimentary deposits with which they are associated, and divides these rocks into 11 classes, corresponding to the Cambrian, Cambro-Silurian, Silurian, Carboniferous, Triassic, and Tertiary series, with five intermediate classes, the latter generally divided again into subclasses. The granitic rocks of different districts in Ireland are then described in some detail, and referred to their places in the proposed chronological scheme.

16. "The Cambrian Rocks of South-east Ireland." By G. H. Kinahan, Esq., M.R.I.A.

The author states that these rocks are greatly altered by metamorphic action. Quartz rock occurs in dykes and other masses among the Cambrian and Cambro-Silurian rocks, but chiefly among the former; it may be foliated and converted into quartzite by what the author calls metapepsis (see preceding paper).

Of the Cambro-Silurian rocks the base is seen only in two places—

at Greenore, and on the S.W. coast of Wexford. At the former it is a fine reddish conglomerate, lying on or against schists; at the latter a massive slate conglomerate. The rocks of this series in ascending order are:—1. Black carbonaceous shales and slates, or grey beds with subordinate beds of grit; 2. Green and grey grits, shales, and slates; 3. The Ballymoney series of green, grey, black, and red grits, sandstones, slates, and shales, with interstratified igneous rocks; 4. Red, purple, and green beds, usually more or less argillaceous.

The Cambrian formation generally consists of green, purple, or reddish grits, shales, and slates, but here and there with grey or even black beds. The author describes the Cambrian rocks in the various areas in which they occur, namely at:—

Howth, where they are but little altered in the N., becoming more altered towards the S.

Bray Head, generally unaltered, and containing many specimens of *Oldhamia*, and with massive dykes of quartz rock.

S.E. Wicklow, where the western boundary is doubtful. Near Carrick Mountain and to the westward the rocks are much altered, and the author thinks that probably masses of Cambrian rocks were forced by disturbances into the Cambro-Silurians, and then the whole were metamorphosed together.

N.E. Wexford. The area commences on the east coast near Courtown Harbour, extends S. to and beyond Wexford, and then S.W. to the coast near Bannow Bay. The rocks are generally submetamorphic, with many large protrusions of quartz rock, generally changed by metapepsis into quartzite. Rooney's Rocks, S. of Poulshore, consist of two protrusions of quartz rock, between and N. of which are green and purplish Cambrian shales, in which *Oldhamia antiqua* has been found, as also in a green bed further south at Cahore. On the coast of Haggard and Bannow the Cambrian and Cambro-Silurian rocks are mixed up very irregularly by means of numerous faults. At Bannow *Oldhamia* is not uncommon. The most continuous sections are seen in this area in the valley of the river Slaney, where the rocks generally dip to the N. at angles of 10°–60° or 80°, and are, going from N. to S.:—

1. Massive grits with some shaly beds, underlain by more or less altered grits and shales; average dip 30°, giving a thickness of about	3000 feet.
2. Schists with quartzites (metamorphosed grits), dip 50°; about.....	4000 „
3. Schists with masses of quartzite (altered quartz rock), dip 40°; about	4000 „
Total about	11000 „

but the numerous faults render the numbers uncertain.

S.E. Wexford. The rocks are more or less metamorphosed, graduating from schist through gneiss into granite near Carnsore.

XLIII. *Intelligence and Miscellaneous Articles.*

ON LIGHT-ABSORPTION ACCORDING TO MAXWELL'S THEORY. BY C. H. C. GRINWIS*.

THE author, in continuation of Maxwell's few remarks on the connexion between the strong absorption of light in metals and their high conductivity for electricity, has further pursued them theoretically:—

Let a plane electrical wave in a body move in the direction of the x-axis with a velocity V and amplitude A. Then let the resulting vibrations take place parallel to the yz-plane and be parallel to the z-axis; let K and μ be the specific induction-capacity of the body for electricity and magnetism, its conductivity C, λ the wave-length; further, for brevity, let k be $=\frac{2\pi}{\lambda}$, and H the magnetic moment along the z-axis. If w denotes the current-intensity, then, according to Maxwell (Treatise on Electricity and Magnetism, vol. ii. p. 394), putting $\mu K=a^2$, $2\pi\mu C=b^2$,

$$\frac{d^2H}{dx^2}=a^2\frac{d^2H}{dt^2}+2b^2\frac{dH}{dt}.$$

If this equation satisfies a periodic function of the time,

$$H=Ae^{-px}\cos k(x-Vt),$$

it thence follows that

$$p=b^2V,\quad V^2=\frac{1}{\mu K+\mu^2C^2\lambda^2},$$

so that

$$H=Ae^{-2\pi\mu CVx}\cos k(x-Vt).$$

If we now calculate from Maxwell's general formulæ (*l. c.* art. 638) the energy contained by the unit of volume of our body in consequence of the above vibrations, we get (since the quantities P, Q, F, and G there occurring are $=0$ when the vibrations are parallel to the z-axis, while H is only a function of x, v, t)

$$a=\alpha=c=\gamma=0,$$

$$b=-\frac{dH}{dx},$$

$$\beta=-\frac{1}{\mu}\frac{dH}{dx},$$

and the electrostatic potential energy E and the electromagnetic actual energy T become:—

$$E=\frac{K}{8\pi}\left(\frac{dH}{dt}\right)^2;$$

$$T=\frac{1}{8\pi\mu}\left(\frac{dH}{dx}\right)^2.$$

* *Verslagen en Mededeelingen d. Kong. Ak. van Wetenschappen te Amsterdam, Naturwiss Abth.* (2) x. pp. 371–383.

For our value of H,

$$\frac{1}{V}\frac{dH}{dt}+\frac{dH}{dx}+pH=0.$$

With insulators $C=0$, consequently $p=0$, $V^2=\frac{1}{\mu K}$; so that then

$$K\left(\frac{dH}{dt}\right)^2=\frac{1}{\mu}\left(\frac{dH}{dx}\right)^2, \text{ or } E=T,$$

and both energies are then always present in equal quantity.

With a conductor, on the contrary,

$$\left(\frac{dH}{dx}\right)^2=\left(\frac{1}{V}\frac{dH}{dt}+pH\right)^2=(\mu K+\mu^2C^2\lambda^2)\left(\frac{dH}{dt}\right)^2+\frac{2p}{V}H\frac{dH}{dt}+p^2H^2,$$

or

$$\frac{1}{8\pi\mu}\left(\frac{dH}{dx}\right)^2=\frac{K}{8\pi}\left(\frac{dH}{dt}\right)^2+\frac{1}{8\pi\mu}\left\{\frac{b^4}{k^2}\left(\frac{dH}{dt}\right)^2+\frac{2p}{V}H\frac{dH}{dt}+p^2H^2\right\},$$

or, if we denote by Δ the last term on the right, which is always positive,

$$T=E+\Delta;$$

consequently T is always greater than E.

To calculate for our case T, E, and Δ and the sum of the two energies ($T+E=W$), we notice that they are periodic functions of t with the period τ. Hence we put the quantity $e^{-px}=U$, and form its mean value by integrating from 0 to τ and dividing by τ; then, putting for shortness $\frac{k^2}{8\pi\mu}=\frac{1}{\sigma}$, we get:—

$$T=\frac{A^2}{2\sigma}\left(1+\frac{p^2}{k^2}\right)U^2;$$

$$E=\frac{A^2}{2\sigma}\left(1-\frac{P^2}{k^2}\right)U^2;$$

$$\Delta=\frac{A^2}{\sigma}\frac{p^2}{k^2}U^2;$$

$$W=\frac{A^2}{\sigma}U^2.$$

The difference Δ between T and E must doubtless be ascribed to the occurrence of currents in the medium. Let us consider the limiting cases.

I. The body is a perfect insulator; C is then $=0$, $b=p=0$, $U=1$; consequently

$$T=\frac{A^2}{2\sigma},$$

$$E=\frac{A^2}{2\sigma},$$

$$\Delta=0,$$

$$W=E+T=\frac{A^2}{\sigma}.$$

II. There exists no electrical polarization; then is

$$V=\frac{1}{\mu C\lambda},$$

$$p=b^2V=2\pi\mu CV=\frac{2\pi}{\lambda}=k,$$

and we have

$$T=\frac{A^2}{\sigma}U^2,$$

$$E=0,$$

$$W=\Delta=T=\frac{A^2}{\sigma}U^2.$$

If Δ then arises from electric currents, it follows that, while the whole of the light is transmitted by insulators, it is entirely absorbed by perfect conductors, and the total store of energy is converted into electric currents.

In the general case, if the energy of the light (that is, that of the electric vibrations) be denoted by L, and that of the electric current by S, we have

$$W=L+S,$$

where

$$L=2E=\frac{A^2}{\sigma}\left(1-\frac{p^2}{k^2}\right)U^2,$$

$$S=\Delta=\frac{A^2}{\sigma}\frac{p^2}{k^2}U^2.$$

Since the factor $U^2=e^{-2px}=e^{-4\pi\mu CVx}$ occurs in the expressions for both energies, both energies continually diminish.

If δ_1 denotes the loss of energy corresponding to L (diminution of polarization), and δ_2 that corresponding to S (which proceeds from the current), the total loss of energy is

$$\delta=\delta_1+\delta_2.$$

Putting, for the sake of abbreviation, $1-U^2=U'^2=2px-2p^2x^2\ldots$, we get:—

$$\delta_1=\frac{A^2}{\sigma}\left(1-\frac{p^2}{k^2}\right)U'^2;$$

$$\delta_2=\frac{A^2}{\sigma}\frac{p^2}{k^2}U'^2.$$

Hence both with conductors (with which $p=k$, $\delta_1=0$) and nonconductors (with which $p=0$) we have

$$\delta_1=\delta_2=0.$$

For small values of x, δ_1 and δ_2 are nearly proportional to x. The losses of electrical energy corresponding to δ_1 and δ_2 are probably the consequence of heat-development, which, accordingly, must always, with the exception of perfect insulators, accompany electrical polarization.

From our formula it further follows that, while light-energy becomes less for undulations with great wave-length λ, and the energy S, on account of the occurrence of currents, is complementary to it, the greater λ is the smaller does the latter energy become.

As the loss of energy is proportional to the total energy, it follows that the same laws hold good for the loss of L and S.

Let us now consider the expression

$$\frac{p^2}{k^2} = \frac{b^4}{a^2k^2+b^4}.$$

We see that when b is small (as it is with bad conductors) $\frac{p^2}{k^2}$ increases with λ increasing; yet the absolute value is small; so that with them the light-energy and its variation are approximately independent of the wave-length.

In bodies in which the polarization is small, $\frac{p^2}{k^2}$ becomes $=1$ nearly; also L and S are then independent of the wave-length, and L is 0 nearly.

In conclusion, let us consider the ratio r of the transmitted to the incident light with a plate of which the thickness is $=l$. The amplitude of the distance l is $AU=Ae^{-pl}$; and

$$r = \frac{L}{E+T} = \frac{L}{W} = \left(1-\frac{p^2}{k^2}\right)U^2 = \left(1-\frac{p^2}{k^2}\right)e^{-2pl}$$

or

$$r = \frac{a^2k^2}{a^2k^2+b^4}e^{-2pl}.$$

In perfect nonconductors (where $b=0$) r becomes $=1$, consequently all the light is transmitted; in perfect conductors (where $a=0$) it is all absorbed. If in r we replace a, b, k, p by their values, we obtain for the relation between the absorption and the quantities K, μ, C, λ:—

$$r = \frac{K}{K+\mu C^2\lambda^2}e^{-4\pi\mu CVl}.$$

In insulators r must be independent of the wave-length; in other bodies, under otherwise like circumstances r increases with the wave-length.—*Beiblätter zu* Poggendorff's *Annalen*, 1877, No. 7, pp. 409–413.

ON SPECIFIC INDUCTIVE POWER. BY V. NEYRENEUF.

The inductive power of insulating substances, discovered by Faraday, has been the object of numerous researches, all of which bear upon the phenomenon of influence properly so called. One might further ask, What modification in the energy of the spark is induced by changing the nature of the insulating plate of a con-

denser? It is this question that I have endeavoured to determine by the following experiments.

Two plane condensers, quite equal and furnished with electrometric appendages, are connected each with one of the armatures of a Holtz machine, on the one side, and, on the other, with the earth. One of them is provided with a plate of glass of 1·32 millim. thickness; the other receives plates of various kinds and thicknesses. The spontaneous discharges always take place at a constant distance. Under these conditions the quantities of electricity translated, during one and the same time, by the number of sparks furnished by each of the conjugate condensers may be regarded as equal.

The following Table sums up the results of a great number of concordant experiments. The number of sparks refers to the interval between two sparks from the standard condenser.

Nature of the plates.	Thickness. millim.	Number of sparks.
Glass	2·15	1·5
„	3·02	2
„	3·75	3
„	5·22	4
Hardened caoutchouc	1	2
„ „	2	4
Vulcanized caoutchouc ..	2	5
„ „ ..	3	6
„ „ ..	4	7
„ „ ..	5	9

The rarer the sparks, the stronger they are. This can be accounted for by the report and the light which accompany them; but it can be demonstrated also by means of a variety of the Kinnersley thermometer in which the action of the spark upon the liquid is replaced by the pushing-back of an index of elder-pith.

It is seen that the ratio of the number of sparks to the thickness of the plate is sensibly constant for plates of the same nature. The irregularities presented by the vulcanized caoutchouc proceed, doubtless, from its want of homogeneity.

It is moreover seen how great are the differences of effect obtained with plates of the same thickness but of different kinds.

Besides, the ordinary laws of the discharge of a condenser are very well verified by employing our conjugate condensers supplied with plates of the same nature. It will be sufficient, in order to comprise in Clausius's formula the peculiarities here signalized, to introduce a constant dependent solely on the nature of the dielectric. This constant, it seems, would be no other than that of Faraday; but it will be remarked that, according to our results, the greater it is the feebler is the discharge.—*Comptes Rendus de l'Académie des Sciences*, September 10, 1877, tome lxxxv. p. 547–8.

ON THE SPECIFIC HEAT AND THE HEAT OF FUSION OF PLATINUM.

BY J. VIOLLE.

I. The specific heat of platinum was measured at 100°, 800°, 1000°, and 1200° upon some pure metal, for which I am indebted to the kindness of M. H. Sainte-Claire Deville.

The mean specific heat between zero and 100°, determined with M. Regnault's classic apparatus, was found to be 0·0323.

In order to obtain the mean specific heat between zero and 800°, the porcelain reservoir of an air thermometer of M. Deville's and an unglazed porcelain vessel containing the platinum mass (423·140 grammes) submitted to experiment were introduced into one and the same horizontal muffle, which was heated with gas in a furnace with a double casing, Perrot's system. When the temperature of the entire apparatus had become quite stationary, the vessel containing the platinum was taken out, the metal withdrawn and rapidly plunged into a platinum eprouvette placed, with the orifice upward, in the midst of the water of the calorimeter. Equilibrium of temperature between the hot platinum and the water surrounding it was slowly established. Care had also been taken to place the calorimeter within an enclosure with a constant temperature, on the model of that adopted by M. Berthelot. The correction for cooling was made by the method indicated by M. Regnault and carried out by M. Pfaundler. Of two experiments thus conducted, one gave 0·0364 at 787°, the other 0·0366 at 780°; therefore the mean specific heat of platinum between zero and 784° is 0·0365.

The mean specific heat between zero and 1000° was obtained in precisely the same manner. An important change, however, was introduced into a portion of the experiments. To avoid the uncertainty which always exists respecting a correction for cooling, although it is small (not exceeding 0°·3 for an excess of 11 or 12 degrees), in certain experiments the platinum eprouvette was omitted and the hot platinum plunged directly into the water: only an insignificant quantity of vapour was liberated; and the time required for attaining the stationary temperature was reduced from fifteen or twenty minutes to a few seconds, which did away with any correction for cooling. The results of twelve experiments (the first three by the old method, the nine others by direct immersion of the platinum in the water of the calorimeter) were:—

0·0376 at 985°	0·0376 at 1002°
0·0379 „ 1028	0·0376 „ 1006
0·0375 „ 991	0·0377 „ 993
0·0376 „ 1005	0·0379 „ 979
0·0377 „ 1023	0·0379 „ 989
0·0377 „ 1023	0·0376 „ 979

whence we have 0·0377 for the mean specific heat of platinum between zero and 1000°.

On replacing the Perrot furnace by another with a double casing,

heated by means of a Schlœsing pipe, we were able to fix and measure temperatures near 1200°. This furnace (constructed, like the first, by M. Wiesnegg) gives even with facility temperatures much higher than 1200°, but of which it has not yet been possible to effect the direct measurement. In the experiments at 800 and 1000 degrees the temperatures, measured with the manometer of the air thermometer, were obtained by bringing the gas to the same volume (making allowance for the variations of volume of the porcelain balloon) at the commencement and at the end of the experiment and noting the variation of pressure. In the present experiments we operated both by variation of pressure and by variation of volume; so that the temperature was measured each time in two different ways. Thus were found:—

0·0388 at 1168°,	this temperature being given by the two measurements			1171° and	1165°
0·0388 „ 1168,	„	„	„	1169 „	1166
0·0389 „ 1194,	„	„	„	1195 „	1192

Therefore the mean specific heat between zero and 1177° is 0·0388.

All these measurements are faithfully summed up in the following formula, which may therefore be regarded as giving the mean specific heat of platinum between zero and t degrees up to 1200°:—

$$C'_0 = 0{\cdot}0317 + 0{\cdot}000006\,t,$$

From this are deduced:—

$C_0^{100} = 0{\cdot}0323$	$C_0^{700} = 0{\cdot}0359$
$C_0^{200} = 0{\cdot}0329$	$C_0^{800} = 0{\cdot}0365$
$C_0^{300} = 0{\cdot}0335$	$C_0^{900} = 0{\cdot}0371$
$C_0^{400} = 0{\cdot}0341$	$C_0^{1000} = 0{\cdot}0377$
$C_0^{500} = 0{\cdot}0347$	$C_0^{1100} = 0{\cdot}0383$
$C_0^{600} = 0{\cdot}0353$	$C_0^{1200} = 0{\cdot}0389$

We have thus the necessary data for the exact measurement, by a simple calometric experiment, of any temperature between zero and 1200°; we have also, by the same, the means of quickly determining any other specific heat—that of carbon for instance, which I have already attacked.

The true specific heat of platinum at t degrees, $\frac{dQ}{dt}$, is, within the same limits,

$$\gamma_t = 0{\cdot}0317 + 0{\cdot}000012\,t,$$

which gives

$$\gamma_{100} = 0{\cdot}0329, \quad \gamma_{500} = 0{\cdot}0377, \quad \gamma_{1000} = 0{\cdot}0437, \quad \gamma_{1200} = 0{\cdot}0461$$

II. The quantity of heat was measured which is given up by 1 gramme of solid platinum from the fusing-point to zero. For this purpose a certain quantity of platinum was melted; into the fused

platinum a wire spiral of the same metal was dipped; and at the instant when the surface began to solidify, a rosette of solid platinum was taken up with the wire and immersed in the water of the calorimeter. With five rosettes, weighing respectively 57·3, 57·87, 81·5, 40·67, and 49 grammes, the following heatings of the water of the calorimeter for 1 gramme of platinum were successively observed—0°·0722, 0°·0704, 0°·0702, 0°·0715, and 0°·0708; mean, 0°·0710. The mass in water of the calorimeter being 1052·524 grammes, we have

$$q = 74{\cdot}73 \text{ units}$$

for the quantity of heat given up by 1 gramme of platinum from the fusion-point to 15°, the mean temperature of the calorimetric liquid in these experiments.

If it be admitted that the specific heat of platinum is represented, up to the fusion-point, by the formula above-given, it follows that, for the fusion-temperature of platinum,

$$T = 1779°.$$

But the increase of the specific heat of platinum with the temperature is without doubt accelerated in the vicinity of the fusing-point, the platinum passing through the pasty condition before becoming liquid; the true temperature of fusion will therefore be slightly below the number thus obtained.

III. By running a certain weight of melted platinum taken as near as possible to the fusion-point, into the platinum eprouvette of the calorimeter, we can measure the total heat of fusion of the metal—that is to say, the quantity of heat necessary to transform 1 gramme of platinum at zero into liquid platinum at the very temperature of fusion. With weights of 47·51, 78·3, 40·82, and 158·79 grammes of melted platinum, the following heatings of the water of the calorimeter, for 1 gramme of platinum, were successively observed—0°·0756, 0°·0757, 0°·0747, and 0°·0767; mean, 0°·0757. The mass in water of the calorimeter being, in these experiments, 1345·42 grammes, we have for the total heat of fusion of platinum, starting from 170° (the mean temperature of the water of the calorimeter),

$$L = 101{\cdot}85 \text{ units}.$$

If from this we deduct the quantity of the heat q necessary to raise 1 gramme of platinum to the melting-temperature, we have the latent heat of fusion

$$\lambda = 27{\cdot}18 \text{ units}.$$

IV. The melting-point of silver, determined in the course of these researches, upon a pure example kindly prepared for me by M. Lory, was found to be 954°, a temperature very near to that given by M. Edmond Becquerel. Other melting-points (those of gold, copper, &c.) shall shortly be measured.—*Comptes Rendus de l'Académie des Sciences*, Sept. 10, 1877, tome lxxxv. pp. 543–546.

THE

LONDON, EDINBURGH, AND DUBLIN

PHILOSOPHICAL MAGAZINE

AND

JOURNAL OF SCIENCE.

[FIFTH SERIES.]

NOVEMBER 1877.

XLIV. *On the apparent Alteration in Weight of a Wire placed East and West and traversed by an Electric Current.* *By* Professor J. W. MALLET, *F.R.S.* *

THE observations of Gilbert, about the end of the sixteenth century, that the earth behaves as a great magnet, the beautiful theory of Ampère, according to which all magnetically polar bodies may be viewed as owing their peculiar character to electric currents circulating round the particles, equivalent in effect to circular currents surrounding the mass as a whole in planes at right angles to the magnetic axis, and the facts observed by Ampère as to mutual attraction and repulsion of conductors conveying currents of electricity serve, as is well known, to explain the directive action exerted, under all circumstances of relative position, by the earth upon ordinary magnets, and also upon movable conductors through which ordinary electric currents are passing.

Thus a magnetized bar of steel, if freely suspended, sets itself (magnetic) north and south, and may be considered as surrounded by circular electric currents which on the lower side of the bar are moving from east to west. And, in like manner, a helix of wire, when traversed by a current from a galvanic battery, if left free to move, sets itself with its axis north and south; and in such position, if we adopt the usual definition for the direction of the battery-current, this current is found to be from east to west on the lower side of the spiral, thus establishing parallelism with the assumed earth-

* Communicated by the Author.

currents, which pass also from east to west on the *upper* surface of the earth beneath.

In one respect, however, the analogy between the earth and a large magnet seems at first sight to fail. If into the neighbourhood of an ordinary magnet we bring a second magnetic bar, or instead of it a spiral wire traversed by an electric current, not only have we *directive* action, tending to render the axes of the bars (or of bar and helix) parallel, but there is also *attraction*, tending to bring the two acting masses together, whence we might expect to find that a magnet, or spiral conductor conveying a current, would also be specially attracted by our earth after taking up the naturally assumed north and south position—or, in other words, that the weight of such mass would, under these circumstances, seem to be increased. Conversely, if two magnetic bars be placed parallel to each other with similar poles adjacent, we have *repulsion*, the currents of Ampère on the nearer sides of the bars being in opposite directions; and so we might look for repulsion by the earth, or an apparent decrease of weight, on the part of an ordinary magnet placed parallel to the earth's magnetic axis, but with reversed poles, or on the part of a helix of wire similarly placed but traversed by a current passing from west to east on the lower side of the spiral. No such appearance of change of weight occurs.

This, however, may be readily seen to arise from the neutralizing effect of the action on one side of the magnet or helix upon that exerted on the other, the difference of distance of the two from the earth as a whole being practically nothing. But if one side could be detached from the other, and action upon the one alone observed, attraction and repulsion ought to be producible. In the case of a magnetic bar this cannot be accomplished, but with a helix it can, one portion of the wire being rendered movable in relation to the rest, while preserving continuity of the electric current. The helix may, of course, for simplicity's sake, be reduced, as in Ampère's well-known experiments, to a single circle, and this to a square or rectangle the sides of which represent the vertical and horizontal components of the current. A straight horizontal wire, then, placed east and west and traversed by a current from east to west, should be attracted by the earth—and if the direction of the current were reversed, should be repelled.

This result was clearly foreseen by Faraday in the course of his early researches on electromagnetic rotation. At the close of his paper of October 1821 *, he says:—"Theoretically,

* Quarterly Journal of Science, xii. 74.

therefore, a horizontal wire perpendicular to the magnetic meridian, if connected first in one way with a voltaic battery, and then in the opposite way, should have its weight altered; for in the one case it would tend to pass in a circle downwards and in the other upwards. This alteration should take place differently in different parts of the world. The effect is actually produced by the pole of a magnet; but I have not succeeded in obtaining it, employing only the polarity of the earth."

In a subsequent paper, of January 1822 *, he examines the point experimentally, saying, after a description † of the mode in which he demonstrated the lateral motion of a wire parallel to itself under the influence of the earth's magnetism :—"Reverting now to the expectation I entertained of altering the apparent weight of a wire, it was founded on the idea that the wire, moving towards the north round the pole, must rise, and, moving towards the south, must descend; inasmuch as a plane perpendicular to the dipping needle ascends and descends in these directions. In order to ascertain the existence of this effect, I bent a wire twice at right angles, as in the first experiment described in this note, and fastened on to each extremity a short piece of thin wire amalgamated, and made the connexion into the basins of mercury by these thin wires. The wire was then suspended, not, as before, from the ceiling, but from a small and delicate lever, which would indicate any apparent alteration in the weight of the wire. The connexions

* Quarterly Journal of Science, xii. 416.

† "A piece of copper wire, about ·045 inch thick, and 14 inches long, had an inch at each extremity bent at right angles, in the same direction, and the ends amalgamated; the wire was then suspended horizontally, by a long silk thread from the ceiling. A basin of clean, pure mercury was placed under each extremity of the wire and raised until the ends just dipped into the metal. The mercury in both basins was covered by a stratum of diluted pure nitric acid, which, dissolving any film, allowed free motion. Then, connecting the mercury in one basin with one pole of Hare's calorimotor, the moment the other pole was connected with the other basin, the suspended wire moved laterally across the basins till it touched the sides: on breaking the connexion, the wire resumed its first position; on restoring it, the motion was again produced. On changing the position of the wire, the effect still took place; and the direction of the motion was always the same relative to the wire, or rather to the current passing through it, being at right angles to it. Thus, when the wire was east and west, the east end to the zinc, the west end to the copper plate, the motion was towards the north; when the connexions were reversed, the motion was towards the south. When the wire hung north and south, the north end to the zinc plate, the south end to the copper plate, the motion was towards the west; when the connexions were reversed, towards the east; and the intermediate positions had their motions in intermediate directions."

were then made with a voltaic instrument; but I was surprised to find that the wire seemed to become lighter in both directions, though not so much when its motion was towards the south as towards the north. On further trial it was found to ascend on the contacts being made, whatever its position to the magnetic meridian; and I soon ascertained that it did not depend on the earth's magnetism, nor on any local magnetic action of the conductors, or surrounding bodies, on the wire. After some examination I discovered the cause of this unexpected phenomenon. An amalgamated piece of the thin copper wire was dipped into clean mercury having a stratum of water or dilute acid over it; this, however, was not necessary, but it preserved the mercury clean and the wire cool. In this position the cohesive attraction of the mercury raised a little elevation of the metal round the wire of a certain magnitude, which tended to depress the wire by adding to its weight. When the mercury and the wire were connected with the poles of the voltaic apparatus, this elevation visibly diminished in magnitude by an apparent alteration in the cohesive attraction of the mercury, and a part of the force which before tended to depress the wire was thus removed. This alteration took place equally, whatever the direction in which the current was passing through the wire and the mercury; and the effect ceased the moment the connexions were broken. . . . . Whether the effect is an actual diminution of the attraction of the particles of the mercury, or depends on some other cause, remains as yet to be determined. But, in any case, its influence is so powerful that it must always be estimated in experiments made to determine the force and direction of an electromagnetic wire acted on by a magnetic pole, if the direction is otherwise than horizontal, and if they are observed in the way described in this note. Thus, at the magnetic equator, for instance, where the apparent alteration of weight in an electromagnetic wire may be expected to be greatest, the diminution of weight in its attempt to ascend would be increased by this effect, and the apparently increased gravity produced by its attempt to descend would be diminished or, perhaps, entirely counteracted."

The results of these experiments of Faraday upon the earth's action on a movable horizontal current have been transferred to all the text-books; and, old as they now are, I know of no essential addition to them, though the mode of theoretically viewing the relation in question has varied a little in different hands. It appears that he did not succeed in directly demonstrating the vertical component of the attraction or repulsion, due to the earth, in the shape of apparent change of weight

of the wire, having in all cases observed vertical repulsion due to another cause than the earth's action—though he does seem to have obtained *an indication* of the result he sought in noticing that this repulsion was "not so much" when the horizontal motion of the wire was towards the south as when it moved northwards. Nevertheless, that a horizontal wire should seem to become heavier when an electric current is sent through it from east to west, and lighter when the current is from west to east, follows so directly from our whole theory of electro-magnetic relations, that years ago, before I had read Faraday's papers above quoted, I had noted down this point as one to be practically tested. I have lately made the experiment, and with a result fully in accordance with theory.

A strip of light dry poplar (*Liriodendron*), 3 metres long, 25 millims. wide and 5 millims. thick, was placed horizontally on edge, and served to support ten pieces of insulated (cotton-covered) copper wire, 1 millim. in diameter, each piece a little longer than the strip, these wires being carefully stretched parallel to each other, five on each side the strip toward the lower edge, and attached to the wood by little cleats at the necessary intervals to prevent sagging. At each end the wires were bent out horizontally so as to leave spaces of about 20 millims. between them, and were then bent downwards at right angles and cut off so as to leave points like the teeth of a rake about 40 millims. long; these points were amalgamated. This system of wires was supported in a horizontal position from one arm of an excellent balance, slender cords attached at several points along the strip being assembled at a single ring, by which the whole was hooked on, and counterpoised.

The total weight was about 505 grms., the balance being capable of bearing a kilogramme in each pan, while turning with a fraction of a milligramme. Two oblong blocks of hard wood were provided, each of which had sunk in the upper surface a row of ten holes, 18 millims. in diameter and 30 millims. deep, at intervals of 20 millims. from centre to centre, to serve as so many independent mercury-cups in which the ends of the long wires should dip; a like number of small holes bored obliquely, and communicating with the larger ones at bottom, served to introduce the ends of the battery-wires. These battery-wires were also insulated, ten in number, and 9 metres each in length, one of them being afterwards cut in two in the middle. They were stretched parallel to each other and near together on a light wooden frame forming three sides of a horizontal square, of which the movable system

of wires formed the fourth side; these sides were laid down on the floor north and south, east and west, respectively, by compass. In the course of the experiments the frame was shifted round so as to make the movable wires occupy in succession the position of each of the four sides. The galvanic battery (Grove's) was placed in an adjoining room; and its polar wires communicated with those of the frame by two single mercury-cups. Ten cylindrical cells were used, in each of which the immersed platinum surface was about 140 square centimetres for each side of the sheet. The current came in at the middle of the side of the square opposite to the suspended wires, passed round to the first of the series of mercury-cups by one of the half-length wires, thence along the first of the ten suspended wires, back around three sides of the square to the second mercury-cup, thence over the second suspended wire, and so on, until it returned to the battery by the second half-length wire, leaving the frame close to the point at which it came in. The whole arrangement of wires was, in fact, a spiral coil of ten turns, distorted into a square, laid down in a horizontal plane, and having one of its four sides free to move up and down vertically while maintaining the current unbroken.

With this apparatus it was found that, when the movable wires were made to run east and west, whether on the northern or southern side of the square, the side of the balance to which they were attached sensibly preponderated if the current (as usually defined) was passed from east to west, and the opposite side went down if the current was sent from west to east. The motion was not simply a momentary impulse, but the disturbance of equilibrium was permanent while the current was maintained. The amount of motion was decidedly greater in the direction of repulsion, or apparent loss of weight, than in the opposite case. In both cases the amplitude of swing of the balance-index was very small, for the obvious reason that a very little rise or fall of the system of wires introduced a serious difference of weight in the shape of disturbed buoyancy of the copper depressed into or lifted out of the mercury. The attempt was made to ascertain what weight would bring back the balance-index to zero after each disturbance; but the measurements were not very satisfactory, in consequence of the clogging of motion by the immersion of the ends of amalgamated copper wire in mercury and the ease with which mercury was taken up or lost in varying amount on their surfaces. The average of the best determinations obtained when the galvanic battery was in full activity was about

·42 grm. for the equivalent of attractive action or apparent increase of weight, and ·56 grm. for that of repulsion or apparent loss of weight. Of course such measurements, even if more accurately made, would apply only to the special conditions of the experiment as arranged.

When the movable system of wires was placed north and south, whether on the east or west side of the square, and whether the current was passed from north to south or the reverse, there was slight repulsion or apparent loss of weight. In all positions slight lateral swings of the movable wires, in all cases in the direction first described by Faraday, were easily observed.

It is proper to notice any conditions of the above experiments which might give rise to misinterpretation of the observed results :—

1. If the movable wires were heated by the passage of the electric current there would, of course, be a tendency to apparent loss of weight by the production of an ascending gaseous current in the surrounding air. This could, however, in no case produce the opposite result ; and in point of fact there was no sensible heating of the wire.

2. The mutual action during the passage of the current between the mercury and the ends of copper wire immersed in it (which Faraday seems to have been inclined to explain by changed cohesive or adhesive relations, and which Ampère proposed to view as evidencing the repulsion of one section of a rectilinear current by another forming its prolongation), acting as it did in the same way at both ends of the movable wires, caused repulsion or apparent loss of weight, thus increasing the effect observed in this direction ; but this cause, again, could never produce the opposite effect.

3. According to the laws of Ampère there was obviously a repulsive action of the wires of all three fixed sides of the square upon the movable system ; and this repulsion involved a small upward vertical component, since the movable wires were suspended at a level a little above the plane in which the other three sides of the square lay. The amount of this tendency to increase of apparent loss of weight must have been very small ; and, as before, no explanation of the opposite *gain* of weight can thence be derived.

4. The only suggestion of possible fallacy as to the apparent *gain* of weight seems to come from the following consideration. If the lateral motion of the wire parallel to itself which Faraday first described be viewed as showing simply a tendency to motion in a horizontal plane, the point of suspension of the

movable wire or wires being fixed so far as horizontal motion is concerned, there would be a lateral *swing* of the turned-down ends tending to lift them partially out of the mercury; and to the extent that, by such lifting, copper in mercury was exchanged for copper in air, there would of course be increase of effective weight brought to bear upon the balance. But measuring the lengths of the balance-index, arm of the beam, and vertical distance from suspending-ring to surface of mercury in which the wires dipped showed, on very simple calculation, that the amount of vertical motion observed would require, to be thus accounted for, not only a far greater amplitude of horizontal swing than was actually seen to occur, but much greater than could possibly occur without being arrested by the wires striking the sides of the mercury-cups.

Thus it appears that in all positions of the suspended wires there was a tendency to upward motion when the current passed; and when the current was from east to west, and the reverse, the apparent gain and loss of weight represented the sum and difference respectively of this tendency with the true vertical component of the earth's action.

It behoves every one who follows in the footsteps of Faraday, and obtains an experimental result in any way different from his, to note carefully in what respect such difference may be due to variation of the conditions observed. In this case, beside the experiment having been made at another part of the earth's surface, and with some difference of intensity of the earth's magnetism, the main points in which the experiment was varied were these:—

1. The substitution of several wires for a single one. This, however, is not essential, as the result was verified afterwards with but one wire.

2. The use of a stronger galvanic current. That employed by Faraday was derived from a single pair of plates of copper and zinc, of the arrangement proposed by Dr. Hare under the name calorimotor; the size of the plates is not given, or the strength of the acid used; but it is stated that the current "would barely warm two inches of any-sized wire." One would hardly suppose the external resistance sufficient to make employment of several pairs of plates important; yet in a repetition of the experiment with a single wire and a Smee's battery of six cells, I found that the effect obtained was distinct with the cells arranged in series, and unobservable when they were coupled so as to form but a single pair of plates.

3. The main reason, however, that Faraday did not obtain

the result expected and sought for is, I believe, to be found in the relative lengths of the horizontal and vertical portions of the movable wire he employed. He does not state these lengths directly for the experiment in which the wire was suspended to a lever-arm, but says, "I bent a wire twice at right angles, as in the first experiment described in this note, and fastened on to each extremity a short piece of thin wire amalgamated;" and from the description of this first experiment it appears that "a piece of wire.....fourteen inches long, had an inch at each extremity bent at right angles;" so that probably, with the pieces of finer wire attached, the turned-down ends may have been each a couple of inches long, while the horizontal portion was only twelve inches, thus making the ratio of the vertical portion of the movable current to the horizontal perhaps $=1:3$, while in my apparatus this ratio, measuring the turned-down ends of wire to the surface of the mercury, = about 1 : 40. In a subsequent experiment to examine the nature of the action which he had noticed between the copper wire and the mercury, Faraday seems to have relatively shortened the horizontal portion of the wire, making it only two inches long; and he then obtained much increased rise of the wire on establishing the current.

It was apparently the opposite step, viz. relatively *increasing the length* of the horizontal wire that was needed to so reduce the disturbing influence as to enable the effect of the earth's magnetism, as originally sought, to be observed*.

There is, of course, nothing new in principle in the experiments above described, the results following directly from what are admitted on all hands as the laws of electro-magnetic action; but it is always interesting to verify for the first time by direct observation any consequence of such well-established laws, and I have been unable to find any record of other work on this particular point except the incomplete, and in a sense unsuccessful, experiments of Faraday which have been quoted.

University of Virginia,
September 5, 1877.

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* I have found that, making the turned-down ends quite short, the experiment may be made to give fairly observable results with a single wire not more than a metre in length.

XLV. *On the Influence of Light on Electrical Tension in Metals.* *By* R. Börnstein *.

RECENT experiments have undoubtedly established the fact that luminous radiation produces on the electrical behaviour of metals an effect which cannot be due merely to an elevation of temperature. This action takes place in two ways, either producing a change in the electrical resistance (a diminution) or a change in the electrical tension. In a former paper † the author has given a summary of the results obtained by other observers with respect to the dependence of the resistance on the illumination. On the subject of a change of electrical tension produced by illumination, experiments have been made by Becquerel ‡, Grove §, Pacinotti ‖, Hankel ¶, and Adams and Day **.

The first four of these observers examined into the electrical phenomena which were presented when, of two plates of the same metal plunged in the same liquid, one was illuminated while both were connected with the terminal wires of a sensitive galvanometer. Under these conditions different kinds of light were found to produce distinct variations in the chemical action; and this difference of chemical action caused the illuminated plate to acquire an electrical state opposite to that of the unexposed one; and consequently an electrical current, which could be measured by a galvanometer, was generated between the two plates. In the papers of Grove, Pacinotti, and Hankel we find descriptions of the changes which took place when conductible heat instead of light was allowed to act upon one of the metal plates. Grove found that heat produced no effect when acting upon one of two platinum plates standing in water slightly acidulated; he attributes the

* Translated by R. E. Day, M.A.

† *Der Einfluss des Lichtes auf den elektrischen Leitungswiderstand von Metallen.* Heidelberg: Carl Winter's Universitätsbuchhandlung. 8vo, 1877.

‡ Becquerel, *Comptes Rendus*, t. ix. pp. 145, 561 (1839); t. xiii. p. 198; *Biblioth. Univ. de Genève*, nouv. sér. t. xxxv. p. 136 (1841); *Ann. de Chimie et de Phys.* (3) t. ix. p. 257 (1843); *Comptes Rendus*, t. xiv. p. 901; *Biblioth. Univ. de Genève*, nouv. sér. t. xl. p. 341 (1842); *Compt. Rend.* t. xxxii. p. 83; *Ann. de Chim. et de Phys.* (3), t. xxxii. p. 176 (1851).

§ Grove, Report of the Meeting of the British Association, Leeds, Sept. 1858; also Phil. Mag. (4) vol. xvi. p. 426 (1858).

‖ Pacinotti, *Cimento*, t. xviii. p. 313 (1863).

¶ W. Hankel, *Sitzungsber. der math.-phys. Kl. der k. Sächs. Ges. d. W.* (1875); *Annalen der Physik und Chemie* (neue Folge), herausgeg. von Wiedemann, Bd. i. S. 402 (1877).

** Adams and Day, Proc. Roy. Soc. vol. xxxv. No. 172, p. 113 (1876).

whole of the effect of illumination to the galvanic polarization produced by the light. Blue light acted much more powerfully than yellow; red light was the weakest; and consequently Grove concludes that these phenomena are due to the chemical and not to the thermal rays of the solar beam, since in the latter case the colours would act in the reverse order. Pacinotti states that, of two copper plates standing in sulphate or nitrate of copper, the illuminated one, when exposed to the rays of the sun, of a petroleum lamp, or to the radiation from a heated iron plate, was always negative to the other. On the other hand, when he placed two small insulated copper boxes of different sizes, one within the other, and filled the space between them and the inner one with water of different temperatures, the warm copper was positive to the colder. Hankel found that warm copper was always negative with respect to cold copper; when two well-polished copper plates were plunged in water, and one was exposed to sunlight, it became negative to the other; and, on the other hand, the more the plates were oxidized or covered with salts, the more did the illuminated one acquire the positive state. One or two Volta's piles were found to give opposite effects according as they were exposed to luminous radiation or to heat. Hankel also experimented with plates of silver, tin, brass, zinc, and platinum; but he describes only the effects of exposure to light, and no experiments with heat.

In all these experiments the electrical currents were produced simultaneously with certain chemical phenomena, and, as is assumed to be the case by some of the above-named physicists, resulted from them. But it appears that electrical currents may be generated by the action of light without any chemical action, in a manner analogous to that of thermoelectric currents, for the production of which no chemical action is requisite.

Currents such as these, which are generated in a simple metallic circuit by the action of light, have hitherto, as far as I am aware, been observed and described only by Adams and Day in the paper above mentioned. They state that, in several of the pieces of selenium examined by them, a partial illumination produced a difference of potential, in virtue of which an electrical current was developed, and, further, that at the points where the platinum connecting-wires were fused into the selenium, illumination produced a current opposite in direction to what a thermoelectric current should have been.

I have endeavoured to connect this peculiar phenomenon with some other metals; and the experiments described in this

paper have shown that exactly the same behaviour is exhibited by the five substances which I have examined, viz. silver, platinum, copper, gold, and aluminium; and therefore it is highly probable that the analogy holds for all other metals. All the metallic laminæ employed were laid upon rectangular glass plates, the two halves of which were coated with different metals. The dimensions of these plates were 100 by 80 millimetres, except the plates coated with platinum, the edges of which were 45 and 70 millimetres in length. The silver was deposited by Martin's method; the platinum was burnt in on plate glass; the copper, the gold, and the aluminium were in thin leaves, such as are used by gilders and may be purchased in the shops. These leaves can be floated on water and then lifted out by means of the glass plate which is to be coated; and then, if the drops of water still clinging to the plate be removed by a gentle heat, the metallic lamina adheres firmly to the glass. In the middle of the plate, where the two metals met, they overlapped to a distance of from 15 to 20 millimetres. Of the different laminæ, the silver appeared blue, the platinum grey, and the gold green by transmitted light, while the copper and the aluminium were not transparent. A chemical analysis showed that the copper contained small quantities of tin and traces of iron; the gold was, as far as could be ascertained, pure; and the aluminium contained traces of iron. For the purpose of making contact with the metallic laminæ, small strips of tinfoil were pasted on to the narrow ends of the glass plates. The layers of silver and platinum were connected with the tinfoil by little strips of aluminium, while the leaves of copper, gold, and aluminium rested upon the edges of the strips of tinfoil and thus completed the electrical contact. Copper wires were soldered to both the strips of tinfoil on each plate. Lastly, strips of black paper were pasted over the junctions of the tinfoil and the metallic lamina which was to be examined, the blackened face being towards the metal, so as to prevent any rays reaching these junctions; and then the plates were ready for an experiment.

The observations were made with a galvanometer having an astatic needle, a mirror, and a scale; and the galvanometer was connected with the plate under examination by a commutator, through which the circuit was completed. The presence of any electromotive force could be unmistakably proved by turning the commutator; and the readings corresponding to reversed positions of the commutator differed always by twice the amount of the deflection to be observed. The position of equilibrium of the galvanometer-needle was

constant, with the exception of very slight variations due to changes of temperature. These variations were so gradual that it was impossible to confound them with any of the phenomena here described, and so much the less as the direction of the deflections due to the behaviour of the metallic plate could be and was altered at pleasure. The apparatus was so sensitive that with a single thermoelectric couple of iron and German silver a deflection of 300 millimetres was obtained on warming the junction with the hand. In this case the distance of the mirror from the scale was about $2\frac{1}{4}$ metres. In commencing operations each of the plates, already described, was covered with a black cloth and left to itself until any possible deflection of the galvanometer had vanished. This precaution was necessary, owing to the fact that, when the different parts of the apparatus had been recently connected, differences of temperature had probably arisen, through the tightening of binding-screws, the warmth of the observer's body, and other causes.

As soon as the galvanometer indicated no change for reversed positions of the commutator, the plate was uncovered, and was then exposed to diffuse daylight, when a small deflection was sometimes observable. This deflection immediately increased when the metallic side of the plate was illuminated by magnesium-light. The true deflections, *i. e.* the semidifferences of the extreme positions of rest of the needle corresponding to reversed positions of the commutator, amounted, when magnesium-light was employed, to from one to four millimetres. After exhibiting this phenomenon, each plate was then warmed by means of a spirit-lamp at the junction of the two metals, and a deflection was thereby produced which was invariably opposite in direction to the previous one, and, in general, greater than it. The plates were usually warmed on the glass side; but there was no difference in the effect when, as was done in a few cases, the flame of the spirit-lamp was brought into actual contact with the metallic surfaces. The connexions between the plate and the commutator were repeatedly changed, in order to make sure that the electrical currents observed on exposure to light originated in the metal plates themselves, and not in any other part of the apparatus. Under these circumstances it was clearly proved that the current generated by the light had always the same direction in each particular plate, and consequently must have originated within it.

Of the five metals here mentioned, nine different combinations of two were examined, and several specimens of each combination were prepared; so that, on the whole, thirty plates,

each consisting of a pair of dissimilar metals, were employed. The different samples of the same combination were so arranged that, as far as possible, each of any two particular metals should sometimes be the upper and sometimes the lower one at the surface of contact; but the results of the experiments gave no indication of this producing any difference. The silver and the platinum, on account of their adherence to the glass, could only form the lower layer in any combination. The tenth possible combination, viz. platinum and silver, could not be prepared.

On warming the junctions, the thermoelectric series of the metals under examination was found to be as follows :—

\+ Silver,
Platinum,
Copper,
Gold,
Aluminium.

In this list the relative positions of the first two metals is assumed from the results obtained by several other observers. It was impossible to determine directly the relative behaviour of silver and platinum.

Under the influence of luminous radiation these metals arranged themselves in the reverse order, viz. :—

\+ Aluminium,
Gold,
Copper,
Platinum,
Silver.

Here, again, the relative behaviour of platinum and silver could only be determined by analogy.

Some experiments were then made with plates consisting of one metal only, the construction of these plates being, in other respects, exactly like that of the previous ones. In one such single plate of gold a current was produced on illumination, and a current in the opposite direction on slightly warming it. In this case we may fairly assume, just as in the experiments of Adams and Day with partially illuminated pieces of selenium, that the substance was not homogeneous, and therefore behaved like a combination of different metals. Other plates, which consisted of silver only, or of aluminium only, showed no electromotive force under the action of light. When, instead of using the magnesium-light, the unrefracted solar rays were allowed to fall upon the plates composed of

two metals, nothing but a thermoelectric current could be detected. This was analogous to the behaviour of illuminated silver plates, whose electrical resistance increased under the influence of the entire solar beam, while it diminished under the influence of particular-coloured rays.

The phenomena here brought forward might possibly admit of an explanation analogous to that for thermoelectric currents. If these latter owe their origin to the fact that the difference of electrical tension at the point of contact of two metals is altered by a rise of temperature, then it is quite conceivable that the difference of tension may also be altered by the penetration of the luminous rays. In this hypothesis we need not assume that the luminous action at the surface of contact of the metal plates penetrates right through the upper plate nor even influences the lower one; the mere illumination of the upper one can modify the tensional difference between the two plates.

Now, in all the experiments referred to in this paper, the luminous radiation produced two simultaneous effects. In the first place, rays were absorbed, and consequently the temperature of the absorbing body was raised; and in this way its electrical behaviour was indirectly affected. But, further, there must have been another kind of action due to the luminous rays, because in these experiments, just as in many of the experiments of other observers, the effects of light and heat were opposed to each other. Now if, in the case of this secondary action, the behaviour of the luminous waves is different from what it would be if they were merely absorbed, then we may perhaps suppose that such rays as pass through the illuminated metal, or at any rate penetrate it to a certain depth, are the direct cause of the observed variations in electrical conductivity and tension, which changes cannot arise from heating. According to this view, it would seem that the more transparent a metal is to a particular kind of light, the greater would be the effect upon it of that light. Now, inasmuch as in this kind of action the rays part with a portion of their *vis viva*, there is here also absorption, but of a different kind from what is usually understood by the term—in which it is generally assumed that the energy is at once converted into heat.

Now, if this attempt at an explanation of the electrical effect of illumination be admitted, then the currents generated by light would correspond in many respects to thermoelectric ones. And this relation might be expressed by calling those currents which are generated by light without any chemical action, photoelectric currents.

If the results thus obtained for the five metals silver, platinum, copper, gold, and aluminium be assumed to hold for metals in general, then the results of this investigation may be summed up as follows :—

In a circuit consisting of two different metals a photoelectric current is generated whenever the two junctions are exposed to luminous radiation of different intensities.

When the same junction is exposed in one case to an increase of temperature and in another to a more intense illumination, the thermoelectric and photoelectric currents respectively generated in these cases are opposed to each other in direction.

XLVI. *On Essential Oil of Sage.* *By* M. M. Pattison Muir, *F.R.S.E., Assistant Lecturer on Chemistry, and* S. Sugiura, *Chemical Student, in The Owens College**.

1. ESSENTIAL oil of sage is obtained by distilling sage (*Salvia officinalis*) with water. The oil upon which we have worked was procured from Messrs. Wright, Layman, and Umney, of London. It was by them believed to be a genuine specimen. We were unfortunately unable to ascertain the age of the sample.

2. The oil was of a yellowish-brown colour, without any shade of green. The smell was intensely sage-like; the taste was hot and burning; the reaction was neutral. The oil did not become resinous, nor did it deposit solid matter on standing in a loosely covered vessel for some months; the reaction remained neutral.

The oil readily absorbs oxygen from the air; about 80 cubic centims. of the sample was allowed to stand in an inverted tube containing air, and placed in sunshine. After two days, the level of the oil in the tube showed that the oxygen (about 4 cubic centims.) contained in the confined air had been entirely removed. On testing the oil with paper soaked in starch-paste and potassium iodide, a blue coloration was produced, but only after some time.

Concentrated nitric acid acts most energetically upon sage-oil, with the production of a red semiresinous body: this action is explosive in its violence if the oil and acid be shaken together.

Strong sulphuric acid causes the production of a brownish-red semiviscid mass; by this action much heat is developed, and sulphur dioxide is evolved. If the semisolid mass be

* Read before the British Pharmaceutical Conference, Glasgow Meeting, 1876; and Plymouth Meeting, 1877. Communicated by the Authors.

allowed to remain at rest for twenty-four hours, and water be then added, and the liquid submitted to distillation in a current of steam, a distillate is obtained, the oily portion of which, when separated from the aqueous part and dried, boils for the most part between 215° and 225°. This distillate appears as a heavy yellow-coloured oil; it is most probably a polymeride produced by the action of the sulphuric acid upon the hydrocarbons present in the original oil.

The greater portion of the product of the action of strong sulphuric acid upon the oil remains behind, after distillation in steam, in the form of a very thick black resin, which becomes almost solid after standing in the air for some time.

The action of dry hydrochloric acid gas upon sage-oil, maintained at a temperature of −10° to −15°, does not result in the production of any solid chlorhydrate. The product, when distilled, boils chiefly at 195° to 205°, but contains only from 1 to 2 per cent. of chlorine, with varying quantities of carbon, hydrogen, and oxygen. If a chlorhydrate is originally formed, it readily undergoes decomposition; the hydrocarbons appear to be partially polymerized by the action of the hydrochloric acid.

A portion of the oil, when mixed with about half its volume of water, the same quantity of strong nitric acid, and one volume of alcohol, became dark red in colour, and after some days separated into an under, light-yellow, and an upper, dark-coloured layer. No solid matter was deposited, however, after twelve months' standing. At the expiry of two months the two layers had reunited.

3. On submitting the oil to distillation, a small quantity of water came over; after the removal of this, distillation began at about 170°; four fifths of the whole quantity of oil distilled between this point and 215°, the greater portion boiling between 175° and 195°. That portion which boiled below 190° was treated with sodium, which caused the formation of considerable quantities of red resinous matter, and again distilled; about four fifths of the whole again passed over below 190°, leaving a semisolid red gelatinous mass, which dissolved in ether to form a brown-coloured liquid with a slight green fluorescence.

The fraction boiling at about 190° deposited a small quantity of solid matter after standing for some time; it was therefore exposed to the cold of several successive days and nights during a rather severe frost, whereby a larger quantity of solid matter was separated.

That fraction, obtained in the first distillation of the oil, which boiled above 190°, was now submitted to fractionation

without being treated with sodium. The greater portion came over below 210°. After repeated fractionation and removal of the solid matter which separated out on standing, the main portion of this liquid boiled between 198° and 203°.

After each fractionation, however, a considerable quantity of resinous matter remained in the flask; and it was only when this had been repeatedly removed that it was found possible to distil the liquid entirely below 203°. It would thus appear that the liquid contained compounds which became polymerized by the action of heat alone; in this respect it agrees with the behaviour noticed in the case of many other essential oils. After repeated distillation over sodium, the fraction which, on the second distillation, boiled below 190°, was split up, for the most part, into two portions:—a smaller, boiling from 156° to 158°; and a larger, boiling from 166° to 168°. During the fractionation a very considerable quantity of yellowish-red resin was formed, chiefly, it seemed, by the action of the sodium upon the oil. This resin was decomposed by agitation with water; the oil obtained was separated, dried, and again fractionated. From the fractions of higher boiling-points a large portion of the solid matter already noticed separated on standing at the ordinary temperature.

In the first distillation of the oil, boiling was discontinued upon the temperature reaching 215°; that which remained was a thick, very dark-coloured liquid. This liquid was now submitted to distillation; about one half distilled below 250°, leaving a semisolid, nearly black mass in the retort. On fractionating the distillate, solid matter was deposited from those fractions which boiled below 220°, but not from the higher fractions. After the removal of all matter volatile below 240° a dark-brown liquid, with distinct green fluorescence, remained in the flask. This liquid was subjected to distillation in a current of superheated steam. About one eighth of the total liquid was obtained in the distillate, the remainder having become almost solid. The distillate, after drying and fractionation, was found to consist almost completely of the solid matter already referred to, held in solution by hydrocarbons.

The oil was thus separated into four main portions:—

(1) A liquid boiling at 156° to 158°.
(2) A liquid boiling at 166° to 168°.
(3) A liquid boiling at 198° to 203°.
(4) A solid deposited chiefly from those fractions of the oil boiling from 190° to 220°.

The resinous matter which remained after the final distil-

lation was very probably produced, or at any rate partly produced, by the polymerizing action of heat upon the original constituents of the oil.

4. That portion of the distillate which boiled from 156° to 158° was fractionated until the greater portion boiled constantly at 157° to 157°·5 (thermometer surrounded with vapour, and barometer at 760 millims.). The liquid so obtained was perfectly colourless; it had an exceedingly slight odour of sage.

We have not subjected this liquid to analysis; but the results of a determination of its vapour-density, and a consideration of its general properties, leave no doubt that it really consists of a terpene, $C_{10}H_{16}$.

The vapour-density was determined by a slight modification of Hofmann's method, which we have described in a paper communicated to the Chemical Society*. The method is easily and quickly carried out, and yields results sufficiently accurate for general purposes.

The following numbers were obtained :—

Height of barometer = 755 millims.
Temperature of air = 17°.
Height of mercury column in barometer tube = 561 millims.
Temperature of vapour = 185°.
Tension of mercury vapour at 185° = 12 millims.
Weight of mercury required to occupy space formerly occupied by vapour = 1018·4 grms.
Temperature of mercury = 20°.
Hence, volume of vapour = 73·28 cubic centims.
Weight of liquid = 0·0682 grm.
Weight of volume of hydrogen equal to volume of vapour under same conditions of temperature and pressure = 0·00101 grm.

$$\text{Hence } \frac{M}{2} = \frac{\cdot 0682}{\cdot 00101} = 67\cdot 46. \quad \text{Calculated} = 68.$$

5. The specific gravity of this terpene was 0·8635 at 15°.

To Dr. Gladstone we are indebted for determinations of the refractive indices of this terpene. We desire to give our best thanks to him for his great kindness.

$\mu A = 1\cdot 4611$. $\mu D = 1\cdot 4667$. $\mu H = 1\cdot 4855$ at 24°·5.

Hence specific refractive energy = 0·0534, and
Refraction-equivalent = 72·6.

6. Dr. Tilden has been so very good as to examine the

* Chem. Soc. Journ. vol. ii. 1877, p. 140.

action of nitrosyl chloride upon this terpene, and to determine the rotatory power of a column of the liquid. The action of nitrosyl chloride is in every respect similar to that observed between the same substance and the terpene from French turpentine oil *. The nitroso-derivative, $C_{10}H_{15}NO$, forms monoclinic prisms of the same form as those described by Story Maskelyne in an appendix to the paper of Tilden referred to:—"The plane ends are replaced by a sort of pyramid, which makes them look more pointed. In general appearance the crystals are not unlike dog-tooth spar†. The melting-point of the nitroso-derivative is 129°; the alcoholic solution of this substance is optically inactive. The specific rotatory power of the sage-terpene is $[\alpha]_D = -37{\cdot}3$.

7. The determinations of the optical properties of this terpene agree very closely with those which have been made for the terpene from French turpentine-oil (terebenthene). Moreover the specific gravity of the sage-terpene is practically identical with that of terebenthene. Riban‡ gives the formula $0{\cdot}8767 - 0{\cdot}0008277\ t$ as expressing the specific gravity of terebenthene at any temperature, t, below 80°. At 15° the specific gravity would be 0·8643. The specific gravity of sage-oil terpene is 0·8635 at 15°. The boiling-points of the two terpenes are also almost identical, probably really identical. As we shall show hereafter, the sage-terpene contained a small quantity of cymene, which would tend slightly to decrease the specific gravity, and slightly to increase the boiling-point of the liquid.

In the following Table we have noted some of the physical properties of terebenthene and of the terpene from sage-oil boiling at 157°:—

	Sage-terpene.	Terebenthene.
B.P.	157°	156°·25 §
Specific gravity at 15°	0·8635	0·8643 §
Refractive indices at 24° for A	1·4611	1·4596 ‖
" " D	1·4667	1·4653 ‖
" " H	1·4855	1·4845 ‖
Refractive energy	0·0534	0·0532 ‖
Refraction-equivalent.....	72·6	72·5 ‖
Specific rotatory power (for soda-flame)	−37·3	−32·4 ¶ (for transition tint).

* See Tilden, Chem. Soc. Journ. [2] xiii. p. 514.
† Extract from letter from Dr. Tilden.
‡ *Comptes Rendus*, lxxviii. p. 288.
§ Riban, *Comptes Rendus*, lxxviii. p. 288.
‖ Gladstone, Phil. Trans. 1863.
¶ Berthelot, *Ann. Chem. Pharm.* lxxxviii. 343.

8. About 20 grms. of the terpene boiling at 157° was surrounded by a freezing-mixture, and concentrated sulphuric acid was added drop by drop, the liquid not being allowed to become warm. A trace of sulphur dioxide was evolved, and a deep-red semisolid mass was formed. After 24 hours this was distilled in a current of steam; the distillate was dried and fractionated; the greater portion boiled between 175° and 178°, and gave the reactions of cymene. On analysis, the following numbers were obtained :—

0·1885 grm. gave 0·6125 grm. CO_2, and 0·181 grm. H_2O.

	Calculated for $C_{10}H_{14}$.	Found.
Carbon	89·55	88·61
Hydrogen	10·45	10·72

A small quantity of this cymene was oxidized by chromic liquor; it yielded terephthalic and acetic acids.

About 7 per cent of cymene was obtained from the terpene.

9. Twelve grms. of the terpene, placed in a flask surrounded with snow and salt, was subjected to the action of bromine, added drop by drop through a narrow tube. The bromine was very rapidly absorbed, a hissing noise being produced on the addition of each drop. When no further absorption appeared to take place, it was found that the liquid weighed 25 grms. In order to convert 12 grms. of $C_{10}H_{16}$ into $C_{10}H_{16}Br_2$, 14 grms. of bromine (in round numbers) are required; 13 grms. were used in the foregoing experiment. The liquid thus obtained was a heavy colourless oil. On submitting it to distillation, torrents of hydrobromic acid were evolved, and a nearly colourless liquid came over, which, however, quickly darkened, until of a reddish-brown colour. On attempting to distil this liquid, it was again decomposed, yielding hydrobromic acid, a distillate boiling from 175° to 180°, another and heavier portion boiling from 220° to 240°, and a considerable quantity of black resin. This process was repeated several times with the same result; nevertheless the greater portion of the liquid eventually distilled between 220° and 240°. That fraction which boiled between 175° and 180° gave all the qualitative reactions for cymene; on oxidation, it yielded terephthalic acid.

Like the other terpenes of the formula $C_{10}H_{16}$, the lower-boiling terpene from sage-oil appears to be readily converted into a dibromide, which is decomposed by the action of heat, with the formation of cymene. This decomposition does not,

however, take place with so great facility as has been noticed in the case of other terpenes of higher boiling-points *.

10. About 25 cubic centims. of the terpene boiling at 157° was subjected to the action of two litres of boiling chromic liquor, containing 10 per cent. of potassium dichromate, and sulphuric acid sufficient to saturate the bases present. After 37 hours the boiling was stopped, and the small quantity of solid matter which had been produced was collected, washed with hot water, dissolved in boiling ammonia, and reprecipitated by hydrochloric acid. It gave the reactions of terephthalic acid. The liquid, when distilled, showed the reactions for acetic acid.

The residue, after polymerizing the terpene with sulphuric acid in the manner described in paragraph 8, and distilling in steam, was boiled for some days in chromic liquor. No solid oxidation-product was obtained.

Wright † has shown that the terpene from orange-peel oil, boiling at 178°, yields no cymene when treated with strong sulphuric acid and distilled in steam, nor does it yield a trace of terephthalic acid on oxidation. The same chemist ‡ has also shown that oil of turpentine yields cymene by treatment with sulphuric acid &c. According to some chemists terephthalic acid is one of the products of the oxidation of oil of turpentine; according to others this acid is not produced on oxidizing that oil. The fact that, when cymene had been removed from the liquid portion of sage-oil boiling at 157°, the residue yielded no terephthalic acid on oxidation, although the original liquid (before treatment with sulphuric acid &c.) did yield this acid, seems to point to the cymene which was present as the source whence the terephthalic acid was derived.

The varying results obtained in the oxidation of oil of turpentine were probably due to the varying composition of the specimens employed; when free from cymene, this oil appears to yield no trace of terephthalic acid on oxidation §.

11. That portion of the oil which, after treatment with sodium and distillation, boiled from 166° to 168°, was fractionated until the greater part boiled constantly from 167° to 168° (thermometer surrounded with vapour; barometer 760 millims.). The liquid so obtained had a somewhat more pronounced odour of sage than the fraction which boiled at 157°; it was perfectly colourless.

* See Wright, "On Isomeric Terpenes," Chem. Soc. Journ. [2] xi. p. 694.

† Chem. Soc. Journ. [2] xi. p. 552. ‡ *Loc. cit.*

§ See W. Carleton Williams, *Ber. deut. Chem. Ges.* v. 1094.

The following are the results of a vapour-density determination of this liquid:—

Height of barometer = 758 millims.
Temperature of air = 18°.
Height of mercury column in barometer-tube = 511 millims.
Temperature of vapour = 185°.
Tension of mercury vapour at 185° = 12 millims.
Weight of mercury required to occupy space formerly occupied by vapour = 874·7 grams.
Temperature of mercury = 20°.
Hence, volume of vapour = 64·61 cubic centims.
Weight of liquid = 0·0804 gram.
Weight of volume of hydrogen equal to volume of vapour under same conditions of temperature and pressure = 0·001129 gram.

$$\text{Hence } \frac{M}{2} = \frac{\cdot 0804}{\cdot 001129} = 71\cdot 2. \quad \text{Calculated} = 68.$$

Two experiments, in addition to that the results of which are detailed, were carried out; but in each a small quantity of air found its way into the barometer-tube; the results were therefore too low. In every case a small quantity of brown resinous matter remained in the small bottle unvolatilized; hence it appears either that the terpene contained a small quantity of a substance boiling very considerably above 185°, or that the action of such an amount of heat as is represented by this temperature exerted a decomposing (polymerizing?) action upon the terpene. The presence of 4 per cent. of a terpene of the formula $C_{15}H_{24}$, supposing this to remain completely unvolatilized, would bring the observed vapour-density to 68·3, which is almost identical with the calculated number.

12. The specific gravity of the terpene boiling at 167° to 168° was 0·8866 at 15°.

We are again indebted to the kindness of Dr. Gladstone for determinations of the refractive indices of this terpene.

$$\mu A = 1\cdot 4588,\ \mu D = 1\cdot 4646,\ \mu H = 1\cdot 4830, \text{ at } 24°\cdot 5.$$

Hence, specific refractive energy = 0·0522, and

Refraction equivalent = 71·0.

13. Dr. Tilden has been so good as to examine the action of nitrosyl chloride upon this terpene. He says, "I could get no solid products from this liquid. The action of the gas caused effervescence immediately; and this is always a bad sign. I suspect this to be a mixture containing a hydrocarbon of the $C_{15}H_{24}$ type. I never got any solid compounds

from these." The specific rotatory power of the terpene boiling at 167° to 168° is $[\alpha]_D = -19{\cdot}9$.

14. The results of the vapour-density determination detailed in paragraph 11 led us to look on the presence of a small quantity of a higher-boiling liquid in this terpene ($C_{15}H_{21}$?) as probable. It might be supposed that the liquid boiling at 167° to 168° is really a mixture of the terpene of lower boiling-point with about 4 per cent. of a terpene of the type $C_{15}H_{24}$ (paragraph 11). Such a mixture—assuming the $C_{15}H_{24}$ terpene to have a specific gravity of 0·915, which is about the mean of the densities of terpenes of this formula as determined by Gladstone, and assuming that no condensation of volume occurred through mixing the two liquids—would have a specific gravity of about 0·865 at 15°; but the liquid boiling at 167° to 168° has a specific gravity of 0·8866 at 15°. The assumption that this liquid is a mixture of the 157° terpene and such an amount of a $C_{15}H_{24}$ terpene as would be in keeping with the result of the vapour-density determination, is therefore not borne out by the actual specific gravity of the liquid. We are rather inclined to believe that sage-oil contains two terpenes of the formula $C_{10}H_{16}$, differing in physical properties, and perhaps a small quantity of a terpene of higher molecular weight.

The physical as well as the chemical properties of the terpene boiling at 157° leave little doubt of the identity of this compound with terebenthene, the terpene obtained from French oil of turpentine. The terpene boiling at 167° to 168° we cannot regard as perfectly pure. In a letter to one of us, Dr. Gladstone says, "The lighter terpene is practically identical with that from turpentine in refraction and dispersion, as well as in boiling-point and specific gravity. The heavier one, with the higher boiling-point, has a lower refractive energy than any terpene I have examined. Is it pure?"

Investigations carried out on larger quantities of oil can alone enable us to make positive statements regarding the composition of the higher terpene.

15. Treatment of the terpene boiling at 167° to 168° with strong sulphuric acid, and distillation of the product in steam, in the manner described in paragraph 8, resulted in the production of about 8 per cent. of a liquid which gave the reactions for cymene, and on oxidation with chromic liquor yielded terephthalic and acetic acids. The polymerized residue yielded no solid oxidation-product on treatment with chromic liquor.

The terpene itself when oxidized, yielded a considerably larger quantity of terephthalic acid than was obtained from the 157° terpene.

A portion of this terpene, when treated with bromine, as described in paragraph 9, reacted in a manner very similar to that already detailed in the case of the terpene of lower boiling-point; only, on distilling the brominated liquid, it was very readily and almost entirely split up into hydrobromic acid and cymene.

16. That portion of the original oil which, upon fractionation, boiled between 198° and 203°, was a nearly colourless heavy liquid, having a very strong odour of sage. It did not become sensibly darker on exposure to the air.

For this liquid, which represents the oxidized liquid constituent of sage-oil, we propose the name of *salviol*. We have analyzed salviol, and have also made a determination of its vapour-density.

I. 0·1664 grm. gave 0·48 grm. CO_2 and 0·162 grm. H_2O.
II. 0·130 „ 0·374 „ CO_2 „ 0·124 " H_2O.

	Calculated for $C_{10}H_{16}O$.	Found.		
		I.	II.	Mean.
Carbon	78·94	78·69	78·46	78·57
Hydrogen	10·53	10·81	10·59	10·70
Oxygen	10·53 (by diff.)	10·50	10·95	10·73

Vapour-density determination.

Height of barometer = 755 millims.
Temperature of air = 17°.
Height of mercury column in barometer-tube = 492 millims.
Temperature of vapour = 185°.
Tension of mercury vapour at 185° = 12 millims.
Weight of mercury required to occupy space formerly occupied by vapour = 788·1 grams.
Temperature of mercury = 17°.
Hence, volume of vapour = 58·16 cubic centims.
Weight of liquid = 0·0786 gram.
Weight of volume of hydrogen equal to volume of vapour under same conditions of temperature and pressure = 0·00107 gram.

$$\text{Hence } \frac{M}{2} = \frac{\cdot 0786}{\cdot 00107} = 73\cdot 46. \quad \text{Calculated} = 76.$$

A small quantity of resinous matter remained in the little bottle at the conclusion of the experiment. The weight of this non-volatile residue was found to be 0·0014 gram. The number given above as representing the weight of liquid taken is the difference between the actual amount weighed out and the weight of the non-volatile residue.

It would appear that the salviol examined was not perfectly pure, or that this substance is decomposed in some way at the temperature to which it was raised, with production of resinous matter. There can, however, be little doubt that the formula $C_{10}H_{16}O$ really represents not only the quantitative composition, but also the molecular weight of salviol.

From the smallness of the quantity of salviol at our disposal we have not been able to carry out further experiments upon this substance.

17. The solid which separated from the higher-boiling portions, chiefly from the fractions boiling from 190° to 220°, has been partially examined by us.

Analysis.

I. 0·112 grm. gave 0·324 grm. CO_2 and 0·104 grm. H_2O.
II. 0·129 „ 0·375 „ CO_2 „ 0·124 „ H_2O.

	Calculated for $C_{10}H_{16}O$.	Found.		
		I.	II.	mean.
Carbon	78·94	78·83	78·86	78·84
Hydrogen	10·53	10·31	10·67	10·49
Oxygen	10·53 (by diff.)	10·86	10·47	10·67

We have not made a vapour-density determination, inasmuch as the results of analysis leave little doubt as to the correctness of the formula $C_{10}H_{16}O$, and the boiling-point prevents the supposition that the molecular weight is represented by a multiple of this formula.

The specific gravity of sage-camphor is greater than that of common camphor, and less than that of borneol. We do not consider the actual numbers obtained by us yet sufficiently trustworthy for publication.

After several sublimations sage-camphor melts at 184° to 186°, and boils at 210°.

This substance crystallizes in monoclinic prisms, ∞P, $-mP$; the crystals are generally rounded off on the prism-edges.

An alcoholic solution of sage-camphor is without action upon the polarized ray.

The appearance, smell, and taste of this camphor closely resemble those of the common variety; sage-camphor, however, has a peculiar sage-like odour, which ordinary camphor has not. Sage-camphor is soluble to a very slight extent in water; it swims upon the surface of water, and exhibits the peculiar rotatory movements of camphor. It is soluble in alcohol (from which solution water precipitates it in the form of white flakes), in chloroform, and in ether. Nitric acid

dissolves sage-camphor with the evolution of small quantities of lower oxides of nitrogen (see paragraph 20). Sulphuric acid dissolves it with difficulty, and hydrochloric acid only after continued boiling.

18. A quantity of sage-camphor was dissolved in chloroform; an equal quantity of bromine was gradually added, the vessel being kept well cooled. Reddish-coloured crystals were almost immediately deposited. The whole was allowed to stand over sulphuric acid *in vacuo* for 12 hours: when the vessel was brought into the ordinary atmosphere the crystals very quickly melted, and hydrobromic acid was evolved in considerable quantity. On standing for several days over sulphuric acid *in vacuo*, crystals were again formed. On distilling the red liquid very large quantities of hydrobromic acid were evolved, a camphor-like solid was deposited, and a considerable portion of the liquid was resinized. The solid camphor-like substance, after several sublimations, melted at 160° to 163°. A similar substance, having the same melting-point, was prepared by treating sage-camphor directly with bromine, washing with caustic soda, and subliming. The melting-point of the crystals increased after each sublimation, until the maximum, 160° to 163°, was attained. During the earlier sublimations hydrobromic acid was evolved.

19. When sage-camphor was distilled in contact with phosphorus pentasulphide, the greater part of the material underwent resination, but a small quantity of liquid was obtained, which, after washing with soda, drying, and fractionating, gave the reactions of cymene; on oxidation with chromic liquor terephthalic acid was produced.

20. A few grams of sage-camphor was dissolved in about 10 parts of concentrated nitric acid, the liquid was boiled for 30 hours or so, the acid was distilled off; the residual semi-resinous matter was dissolved in hot water; the solution was boiled down and set aside. A small quantity of a colourless, indistinctly crystalline body was obtained. This substance melted at 172° to 176°. The quantity at our disposal was too small, and not sufficiently pure, to allow of accurate analyses being made; the numbers which we did obtain agreed as closely as could be expected with those required by the formula for camphoric acid — $C_{10}H_{16}O_4$.

21. Sage-camphor is almost certainly an isomer of common camphor; its melting-point, boiling-point, and other physical properties, however, as also the difference of its behaviour towards bromine, prevent us from believing that it is identical with common camphor.

22. Our investigations are not sufficiently complete to

allow us to enter into theoretical discussions concerning the structural formula of camphor and the substances related to it; nor can we venture to make any generalizations concerning the members of the terpene group. Both of these subjects are of much interest. We purpose to prepare much larger quantities of the terpenes, salviol, and sage-camphor, and to determine the physical and chemical properties of these bodies, combining this investigation with a research into the constitution of the camphors in general.

We take this opportunity of again returning our best thanks to Drs. Gladstone and Tilden for their kindness in examing the optical and other properties of the two sage-terpenes.

XLVII. *On the Lower Limit of the Prismatic Spectrum, with especial reference to some Observations of* Sir John Herschel. *By* Lord Rayleigh, *F.R.S.**

ALL theoretical investigations into the laws of dispersion have led to the conclusion that, as the wave-length of light increases, the refractive index for a given substance approaches a finite limit, below which it cannot pass. According to Cauchy, the refractive index (μ) can be expressed approximately as the sum of two terms; of which the first is constant and coincident with the limiting value just spoken of, while the second varies inversely as the square of the wave-length (λ). This law, which may be expressed $\mu = A + B\lambda^{-2}$, agrees very well with observation over the less-refrangible part of the spectrum, and may fairly be extended to the ultra-red rays; so that, apart from all theory, there is good reason for thinking that μ cannot fall below a certain value, however great the wave-length may be.

In estimating the place of the limit on any particular map of the spectrum, we must bear in mind that in ordinary prismatic spectra equal distances do not correspond to equal differences of μ. The prismatic spectrum as seen at one view through a prism of considerable angle depends, not only upon the material and angle of the prism, but also upon the actual position in which the prism is placed. Thus different spectra are obtained according to the ray selected for minimum deviation: if the green ray pass with minimum deviation, the deviations of the extreme rays of the spectrum are greater than if the prism were set specially for them, and thus the red end of the spectrum is unduly compressed and the blue end is un-

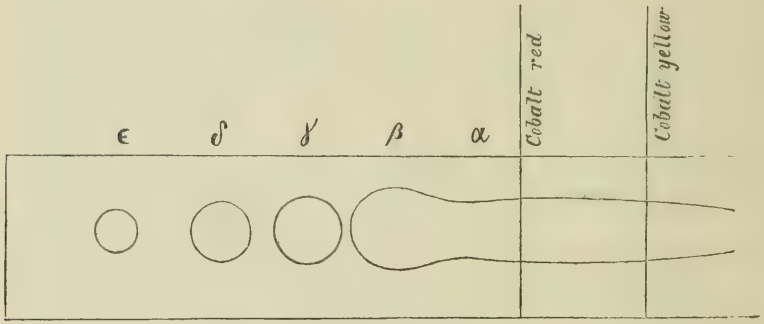
* Communicated by the Author, having been read in substance before the British Association at Plymouth, August 1877.

duly dilated. In order to obtain a map independent of any particular setting of the prism, it is necessary to readjust to minimum deviation for each ray that is observed. But even this map depends upon the refracting-angle.

The best representation of the prismatic spectrum for theoretical purposes is one in which the position of a fixed line measures its refractive index (which may be calculated in the ordinary way from the observed value of the minimum deviation). If we then erect ordinates inversely proportional to the squares of the wave-lengths of the principal fixed lines, the points thus determined will be found to lie very nearly on a straight line, whose prolongation cuts the spectrum at the limit of refraction. In the case of an ordinary spectrum the line determined in this way is curved, and its prolongation cannot be made with the same confidence ; nevertheless there is no difficulty in marking approximately the required limit.

In the 'Philosophical Transactions' for 1840 there is a very interesting memoir by Sir John Herschel, in which he described an ingenious method of obtaining a thermal spectrum. The solar rays were received directly on the prisms without the intervention of a mirror or slit, and after refraction were collected to a focus by an achromatic lens of 25 inches focal length. Two flint-glass prisms of 45° in the position of minimum deviation were employed; and the apparatus was driven by clockwork so as to follow the apparent motion of the sun. In the focus of the lens was placed a strip of thin paper, of which the hinder side had been carefully blackened with indian ink, or (preferably) with the smoke of oil of turpentine. When all was ready for an experiment, the clean side of the paper was washed over rapidly with strong spirits of wine, the effect of which was to render the paper transparent so as to allow the smoke to show through. As the alcohol evaporated under the influence of the thermal rays, the paper gradually recovered its whiteness. "After a few minutes a whitish spot begins to appear considerably below the extreme red end of the luminous spectrum, which rapidly increases in breadth until it equals the breadth of the luminous spectrum, and even sometimes surpasses it—and in length until it forms a long appendage exterior to the spectrum, and extends moreover within it, up to and beyond the fiducial yellow. In this state, and just as the general drying of the paper begins by whitening the whole surface to confuse the appearances, a second, sudden and copious, wash of alcohol from above downwards must be applied, without disturbing the spectrum or in any way shaking the apparatus. The superfluous alcohol will have hardly run off when the phenomena of the thermic spectrum will begin

to appear in all their characters—at first faintly, and, as it were, sketched in by a dimness and dulness of the otherwise shining and reflective surface of the wetted paper; but this is speedily exchanged for perfect whiteness, marking by a clear and sharp outline the lateral extent of the calorific rays, and by due gradations of intensity in a longitudinal direction their law or scale of distribution both within and without the luminous spectrum."



Herschel's Thermal Spectrum.

Sir John Herschel thus describes the results:—"The most singular and striking phenomenon exhibited in the thermic spectrum thus visibly impressed, is its want of continuity. It obviously consists of several distinct patches, of which α, β are the most continuous and intense, but are less strongly separated, and of which, when the sun is very strong and clear, it is even difficult to trace the separation. The spot γ, on the other hand, is round and well insulated; it begins to appear on the paper soon after the ovals α, β are fully formed, and when β has assumed a sharply rounded outline. The first symptom of its appearance is the dulling of the wet and shining surface of the paper, which is speedily followed by the appearance of a small round white speck; this continues to increase rapidly in size and whiteness, and at length assumes a definite and perfectly circular outline, within which the paper is entirely white. By degrees the oval β and this spot join and run together, forming a white streak deeply indented at the point of junction. It is not till this happens that similar symptoms begin to betray the existence of a still more remote spot, δ. Indeed it generally requires another wash of alcohol before this can be fully brought into evidence. It is, however, perfectly unequivocal, though very much feebler and rather worse-defined than γ, with which also it is somewhat better-connected than γ with β. Of the existence of a still

more remote spot I have hardly a doubt; but it is very difficult to obtain a sight of it."

Another method, also discovered by Herschel, depends upon the use of papers prepared with red prussiate of potash and perchloride of iron. The mixed solution (which, if the salts are pure, is at first free from green or blue precipitate) is washed over paper under the influence of the spectrum. The thermal rays manifest themselves by a brown coloration, which afterwards changes to blue. The action of the blue and violet rays is purely photographic, and produces at once the deposit of prussian blue; but the impression of the ultra-red appears to be due rather to thermometric heat. In this way Herschel obtained a representation of the thermal spectrum "as far as δ, with even some trace of ϵ"*.

Notwithstanding this concurrence of evidence, there is great difficulty in accepting Herschel's result. The heat-spots δ and ϵ are decidedly beyond the position at which dispersion should cease; and it is doubtful whether there should be thermal effect even so far down as γ. I have examined one of Herschel's spectra† in which the positions of the fixed lines are indicated, and find for the limit of refrangibility a position close to the spot γ; but the data are hardly precise enough for more than a rough estimate.

Wishing, if possible, to find the explanation of the discrepancy, I have made many attempts to repeat Herschel's experiments, but without obtaining any evidence of thermal action nearly so low down in the spectrum as that recorded by him. The sun's rays were reflected horizontally by a silver-on-glass mirror, or by a piece of common looking-glass, into a darkened room, where they fell upon the prism. In order to obtain a spectrum of about the same purity as Herschel's, I generally employed a bisulphide-of-carbon prism of 60°, giving a beam containing about three square inches of light. The prism was placed in such a position as to give minimum deviation for the extreme red. To collect the rays various lenses were tried, including a single lens of 24 inches focus and a photographic portrait-lens of about 8 inches equivalent focus, the latter of which gave an exceedingly intense spectrum. In some experiments a heliostat was employed; and in others the solar image was kept nearly in one place by hand. In order to guide the eye, the waste light reflected from the first face of the prism may be collected to a focus by a suitable lens and thrown upon a small hole in a piece of card. Even a small apparent motion of the sun will then give rise to a reappearance of light at the

* Phil. Mag. vol. xxii. (1843).

† Photographic News, September 9, 1859.

edges of the hole. In experiments such as the present, where intense spectra are required, it is often better to dispense with a slit; but it then becomes more important than ever to get rid of the apparent motion of the sun.

For fixed points of reference I followed Herschel in using the nearly definite rays insulated by cobalt glass, of which the principal are the extreme red, and a ray in the yellow nearly halfway from D towards E*. After the spectrum had impressed itself the glass was held to the eye, and the positions of the centres of the red and yellow images of the sun marked with a fine pricker or pencil.

When the light is intense, the thermal spectrum begins to show itself ons moked paper in ten or twenty seconds; and the experiment is one of great beauty, which I desire to recommend to those who have access to a clear sun and are in possession of the necessary (very simple) apparatus. The second method, with the iron salts, has the advantage of giving permanent results, which can be examined at leisure. Both methods agreed in giving thermal spectra ending on the less-refrangible side in a more or less detached spot, whose position, however, does not coincide with any of Herschel's. On the contrary, its centre falls almost exactly in the gap between Herschel's β and γ. The gap by which the final spot in my experiments is separated from the remainder of the spectrum is almost exactly as far below the centre of the red cobalt image of the sun as that is below the centre of the yellow image, coinciding therefore with the centre of Herschel's spot β. The most careful attention, in combination with frequent repetition of the experiment, has failed to give me any indication of still less-refrangible rays. In order to vary the conditions I have used a glass prism of 60°, a rock-salt prism and lens (in conjunction with the silver-on-glass mirror), and, finally, a large bisulphide-of-carbon prism of 45° (made for me by Ladd) which gives a beam nearly 16 square inches in area, but without success.

At the same time I cannot pretend to feel entire confidence in these results. Herschel was an experimenter of great skill and experience, whose carefully recorded conclusions cannot be put aside without explanation. It has occurred to me as barely possible that a source of error lay in light reflected internally at the base of Herschel's prisms. It is known that the regular spectrum of an isosceles prism with a polished base is accompanied by a white image, due to light three

* A certain thickness of the absorbing medium is necessary. The piece I use is sufficiently wedge-shaped to allow me to choose the most suitable thickness, which varies to some extent with the light.

times reflected, whose position is the same as that part of the spectrum which passes with minimum deviation*. I am informed by Captain Abney that the bases of Herschel's prisms were polished, which is so far in favour of this view. Nevertheless I feel great hesitation in suggesting such an explanation, and only do so in default of any other. I should be very glad if some other experimenter could be induced to undertake an examination of the subject, and would willingly furnish for comparison specimens of the spectra that I have myself obtained.

Terling Place, Witham,
September 1877.

XLVIII. *Preliminary Communication on Electric Discharges through Rarefied Gases.* By Eugen Goldstein†.

During an investigation on luminous discharges through gases, which I was able to make in the Laboratory of the Berlin University, I have arrived at the following results.

1. We cannot maintain any more the distinction which has been drawn between the positive and negative lights; nor is it probable that the positive discharge is analogous to the metallic or electrolytic conduction, as has been stated. Positive and negative light are of the same kind; and it is possible to connect them by a continuous series of intermediate stages. I retain, however, for the present the name negative light for the phenomenon in which the properties which have been hitherto supposed to be characteristic of the light at the negative pole are prominently brought forward.

I have been able to give, by a suitable experimental disposition, all properties which are supposed to belong to the negative light only, to the positive discharge, with the sole exception of the peculiar stratification of the negative light.

Such properties are, for example, colour and spectrum of the negative light, its behaviour in the magnetic field, the power to produce fluorescence, the formation of the dark space, &c.

2. I call the space in a vacuum-tube which is situated towards the negative pole the negative space. My results are, then, as follows:—

The properties of the discharge between the positive pole and the dark space depend on the alteration in the cross section of the conducting gas. If the cross section increases

* Helmholtz, *Physiologische Optik*, p. 263.

† Translated by Dr. Arthur Schuster from a separate copy of the *Monatsberichte der Akademie der Wissenschaften zu Berlin*, May 4, 1876.

from the positive towards the negative pole, the properties are those of the so-called positive light. If, on the other hand, a rapid diminution of cross section takes place in the direction of the current, the discharge at that point will have all the properties of the negative light. The more rapid this diminution is, the more like a negative light will the discharge appear. By varying in different ways the cross section, we can form the intermediate stages between the positive and negative light.

3. Between the dark space and the negative pole we always see the negative light.

In a series of experiments it appeared as if the passage of electricity from the electrode to the gas took place through a series of fine pores. Without putting forward any hypothesis, I merely draw attention to this fact in order to show that my statement, as to the variation in cross section being the primary cause of the distinction between the two discharges, is not in disagreement with the appearance of the negative light at the negative pole.

The distinction which has been drawn between the two parts of the discharge which lie on either side of the dark space took its origin in the difference between their optical and magnetic properties.

4. A large number of observers agree in the statement that the spectrum of a gas at the negative pole is different from that of the positive discharge. Such differences seem to have been made out with certainty in the case of nitrogen and hydrogen.

Experimenting with these gases, I succeeded in changing the spectrum of the positive discharge into that of the negative light, either by great exhaustion or by an increase in the intensity of discharge.

5. The observations of Reitlinger and Kuhn, "On Spectra of Negative Electrodes and of Geissler Tubes which have been used for a long time" (Pogg. *Ann.* vol. cxli.) are entirely explained by the fact that the gas, owing to the long-continued discharge, was absorbed by the electrodes. Owing to the great exhaustion thus obtained, the spectrum of the negative pole was seen throughout the tube.

I have often found tubes which gradually absorb the gas contained in them; and I have now some in my possession, in which I can at pleasure produce the phenomena either of great exhaustion or of high pressure. By heating up the electrodes from outside, the gas is driven out of the electrode and the pressure increased. The passage of the currents, however, soon causes the reabsorption of the gas, and consequently the phenomena of great exhaustion appear again.

6. Since Plücker's time it was believed that, while the negative light sets in magnetic curves in the magnetic field, the stratified positive light behaves like a solid conductor fixed at both ends, and is accordingly deflected according to Ampère's law (Hittorf). I have found that the positive light behaves in the magnetic field exactly like the negative light; a smaller force even is necessary to set the positive light into the curves than that required to do the same for the negative light.

In order to show this behaviour of the positive light, it is only necessary that the vessel containing the gas should have such a shape and position that its curvature at the points of contact with the lines of magnetic force would be greater than the curvature of the line of magnetic force at the same point. Only when this condition is fulfilled can the discharge set into the magnetic curve without touching the vessel.

7. Only the immediate neighbourhood of the positive pole seems to be distinguished by a peculiar behaviour in the magnetic field. At the negative pole the magnetic force, as shown by Plücker, gives rise to a sheet which is situated axially. At the positive pole, under great exhaustion, a similar sheet appears surrounding an equatorial electrode; but its position is equatorial. If the electrode has the usual form, the sheet is of an oval form and consists of three parts. The first part, which is the one next to the electrode, is nearly elliptical, and does not give out any light; the two remaining parts surround the first one in two spiral curves. If the position of the positive pole is axial, a cylinder of light is seen which is also separated from the metallic surface by a dark space.

8. The form which the electric light assumes in the magnetic field depends on the quantity of electricity which passes in each discharge. Intense discharges, such as we obtain by introducing air-spaces in the outer circuit or by means of condensers, show phenomena which have not hitherto been observed. Whatever the form of the tube is in which these discharges take place, the phenomena are essentially the same as in simple cylindrical tubes the electrodes of which coincide with the axis of the cylinder.

For simplicity's sake I refer, therefore, all phenomena to such cylindrical tubes. I call an axial position any position in which the axis of the cylindrical tube is parallel to the line joining the magnetic poles. The tube may either be situated above or by the side of the magnetic poles. The tube is supposed to be longer than the distance separating the two poles of the magnet.

The discharges, under these circumstances, always take the form of a Z, the plane of which is equatorial or axial, accord-

ing as the position of the tube is equatorial or axial. One of the two arms of this figure is always more or less narrow, and pressed against the wall of the tube; the other arm is wide, and in the equatorial position spread out like a sail. This sheet appears continuous if the discharges are not very strong; if the discharges are strong, it breaks up into distinct magnetic curves. If the discharges are very intense the two arms are separated, and we have the appearance which I have described in a former communication as the magnetic effect on "thick sparks"*.

The inclined bridge between both arms of the figure appears also in the form of a wide sheet made up of magnetic curves. The narrow arm joins this bridge to the positive pole, the wide arm to the negative pole. If the tube is shifted parallel to itself, the position of the bridge shifts towards the other side.

9. The phenomenon just described allows us to convince ourselves that the magnet can set parts of the positive light into magnetic curves. If the positive pole lies in the line joining the poles of the magnets, the positive light close to the pole sets into the lines of magnetic force. I have also investigated the green light which appears on the glass under certain circumstances, chiefly round the negative electrode.

10. I have found that this luminosity of the glass is rather due to phosphorescence than to fluorescence, as it lasts a good deal longer than the discharge. The colour of this light may even change during its existence, as it does in a common glass, from green towards a yellowish red.

11. The negative light which produces this phosphorescence is, as Hittorf has already assumed, propagated in straight lines which emanate from the electrode into the surrounding space. I have been able to confirm this by many experiments. There are, however, phenomena which distinguish this propagation in straight lines from others which also take place in straight lines like that of light. Hittorf has observed that a body situated between an electrode which has been reduced to a point, and the walls of the glass, throws a shadow on the wall in the phosphorescent light. But even if the electrode consists of a sheet of some extension, we can obtain well defined, though not absolutely sharp shadows of bodies which are not too far away from the electrode. A simple sheet of light emanating from the electrode would only throw a hardly visible penumbra on the wall.

Every surface-element of the negative pole, instead of radiating equally towards all sides, only sends out a small cone of light, the axis of which lies in a direction normal to the sur-

* Phil. Mag. May 1875.

face, and the aperture of which never amounts to more than a few degrees. If the electrode, for instance, is formed by a thin wire, the negative light surrounds it in the form of a spheroid; through the spheroid a small assemblage of cones may be seen more luminous than the rest. The negative light extends therefore in straight lines from the electrode, and from each element of the electrode, chiefly in a direction near the normal.

12. Let us now assume that the pressure and intensity of discharge are such that the wall surrounding the negative electrode shows the phosphorescent light. If an additional wire, not connected with any source of electricity, is introduced parallel to the electrode, its shadow will appear on the surrounding wall. The shadow will consist of a small and sharp dark line on the phosphorescent glass. As soon, however, as we connect the second wire with the electrode, so that we have a double negative pole, two dark and well-defined fields will be seen to replace the linear shadow. These fields are bisected by a plane passing through the electrodes. The form of these fields is that of a rectangle the longer sides of which run parallel to the electrodes, and the shorter sides of which are replaced by a curve convex towards the exterior. These and some other phenomena, to be described in another communication, are explained by the following experimental facts.

The negative electrode is the seat of a repulsion, which deflects every line of flow passing near it away from the electrode. I have convinced myself by special experiments that these lines of flow are straight lines until they nearly reach the electrode; they are then almost suddenly deflected, so that they assume the form of a branch of a hyperbola.

13. The phosphorescent light of the glass produced by the negative discharge is but seldom of uniform intensity, and sometimes shows very strange patterns. One can always show that the light depends on the form of the surface of the electrode. The cause of this effect of the electrode is the deflection of lines of flow which I have just mentioned. Lines of flow coming from one part of the surface and passing near other elements of the surface are deflected by it, and cause the appearance of a pattern on the glass tube. This explains the fact that patterns stamped into the electrode show themselves in the phosphorescent light on the glass wall. I mention, for instance, the head of a coin which was used as a negative electrode, and which appeared with every detail on the glass wall in the phosphorescent light, even if the wall was at a distance of several centimetres.

I now pass to a few observations on stratifications.

14. The stratification of the positive discharge shows a continuous variation of forms, the first and last of which have little resemblance to each other. One extreme form represents the stratification as it was first observed, and which is generally known: it consists of a series of narrow disks of light separated by small and dark intervals. The other extreme form shows long columns of light, the length of which is sometimes a hundred times that of the former kind; these long columns follow each other closely; the beginning of one and end of the other is chiefly marked by the fact that the different poles of one stratification have a different intensity.

The two kinds of stratification may appear in the same tube. The first kind corresponds to the pressure at which the stratification first appears on exhausting the tube; the other form corresponds to the lowest pressures at which the stratification is still visible. Different gases show also variations in the form of the stratification which first appear on exhausting the tube.

15. The brightness of each stratification is not uniform. It has a maximum at its negative pole and decreases towards the positive pole, quickly if the length is small, more slowly if the stratification is long.

16. Besides the unsymmetrical distribution of brightness, one and the same stratification shows sometimes differences in colour. These differences are sometimes not only differences in tint merely, but two colours which stand in strong contrast to each other may succeed each other—for instance, red and blue or yellow and blue. One stratification may even show more than two colours.

A variation in pressure causes a variation in the colour of the stratification. The changes are more or less striking, according to the nature of the gas. Hydrogen, for instance, which was prepared by means of zinc and sulphuric acid and purified in the usual way, though not absolutely without odour, showed successively the following colours in one stratification as the tube was exhausted:—first, half blue and half pink; then entirely blue; then half yellow and half blue; then entirely grey. The length of the stratification was about $1\frac{1}{2}$ to $2\frac{1}{2}$ centims. If the hydrogen was readmitted and then exhausted again, the same variations reappeared in the same order.

17. A closer study of the behaviour of stratification leads to the conclusion, that the various positive stratifications which appear simultaneously in a tube which is of the same width throughout are not equivalent. They differ from each other in the same way, though not to the same degree, as so-called positive light from the negative light.

18. Differences in thickness, curvature, mobility, are easily observed. These differences are strikingly shown by the colour of the different stratifications. Just as one and the same stratification may have different colours in different parts, the different stratifications of the same discharge may vary in colour.

In a tube filled with hydrogen I saw, for instance, the first stratification blue, the second pink, the third half blue and half pink. A variation in the pressure, as I have said, varies the colour of each stratification; but each stratification shows a different variation.

19. I shall not here enter into various combinations which may thus be obtained; but it is clear that the statement that one and the same gas shows always the same colour if rendered luminous by the electric discharge is wrong. The discharge may show a great variety in colour for the same gas, even if the cross section of the tube be constant throughout.

Different spectra must correspond to the different colours, though in some cases such a difference may only be due to difference in the relative intensity of the different parts of the spectra.

It follows that for the same gas, the same pressure and cross section of the tube, and intensity of discharge, the spectrum may yet be different.

20. One is tempted, of course, to look for the cause of these differences in the irregularity of the tube or the impurities. I shall give, further on, the proof that the real cause lies deeper, and that there is a law regulating these differences.

If we number each stratification, calling the one next to the negative light "1," we can say that the character of each stratification is a function of its number.

21. The stratification of the positive light is, in all cases which I have examined, the better defined the nearer it is to the negative side of the positive light. This is true for whatever the shape of the tube may be. The gases which I have examined are air, hydrogen, nitrogen, carbonic oxide, carbonic acid, aqueous vapour, alcohol, ether, and metallic vapours.

22. The stratification need not extend along the whole of the positive light; in the same gas the column of light is stratified to the greater length the wider the tube is.

23. If a tube is composed of various parts, each part behaves like a separate tube which has its electrodes at the two points of entrance of the current. I shall call these points secondary poles. Behind each secondary negative pole the stratifications begin again with fresh definition, even if they are almost un-

distinguishable on the other side towards the metallic negative electrode, owing to the great length of the column of light.

24. I may be allowed to draw attention to the fact that the laws which regulate the character of discharge through each part of the tube (*cf.* also my paper already referred to) enable us to predict all phenomena which tubes of any complicated shape and form may present under any pressure, as soon as the phenomena are known which are presented by tubes having the form of the parts which make up the tube under consideration.

The knowledge of the phenomena seen in tubes which have the form of cylinders, spheres, or ellipsoids is sufficient to predict everything that can be seen in all tubes which have hitherto been made, in the most complicated ornamental tubes as well as in simple spectral tubes. I reserve a more detailed explanation and application of the facts.

25. If a cylinder is divided into one part containing the negative pole and into several other similar parts communicating with each other by small holes, each part will behave like a separate cylindrical tube. At its negative pole it will give out light which has all the properties of the negative light; and the remainder of the part will be filled with positive light up to the secondary positive pole. If the light is stratified, we must number the stratifications in each part separately.

If we fill, for instance, the tube with a gas showing stratifications (say, hydrogen), we obtain effects like those described above—stratifications showing different columns, and columns of stratification made up of parts of different colours.

The colour and form of the different stratifications, however, repeat themselves exactly in the same order in every part. Each stratification in each part corresponds to another stratification in every other part which has the same properties as regards colour, brightness, size, &c. The corresponding stratifications are those which have the same number. Stratifications of the same number, and only those, are entirely alike.

26. It also follows that by introducing a series of rapid changes in the cross section the dark space which has hitherto only been observed near the negative electrode can be obtained as often as we like*. By choosing a suitable shape of tube, we can make the electric discharge pass in a non-luminous path through almost any distance.

In a tube 30 centims. long, 25 centims. may be, for instance, entirely non-luminous if the tube consists of a short part con-

* In a so-called funnel-tube Poggendorff has already observed a series of dark spaces (Pogg. *Ann.* vol. cxxxiv. p. 2).

taining the metallic electrode and two cylinders communicating with each other by narrow channels and about 6 centims. wide.

27. I have already mentioned that a continuous transition may be established from positive to negative light. This can be shown in the following way. I have said that a rapid diminution in the cross section in the direction of the positive current produces a negative glow at that point. If in a tube presenting such rapid changes, the variation in the cross section is gradually diminished, so that the tube gradually assumes the shape of a tube of uniform width, the negative glow gradually assumes the shape of a positive stratification, and the dark space which always forms the boundary to the negative glow gradually passes into the dark space which separates the different stratification.

The same result may be obtained with one and the same tube by varying the pressure of the gas. If the variation in cross section is not too rapid, the negative glow extending from the narrow into the wider part gradually loses the characteristic properties of the negative glow on exhausting; and, finally separating entirely from the narrow part and passing into the wider parts, it forms the first positive stratification.

I may state these results in the following words; but as a matter of precaution, I limit the statement to the longer stratifications, excluding the short and oscillating ones, which cannot easily be subjected to accurate observation:—

Each stratification of the positive glow corresponds to the so-called negative glow which surrounds the negative electrode; the stratified positive discharge is therefore only a succession of negative glows.

28. We may also look at the negative glow as a simple stratification.

This new way of looking at the negative light allows us to draw many conclusions, especially if we combine with it another law.

29. This law may be stated in the following words:—The interval between the ends of two stratifications for a given pressure and intensity of discharge depends entirely on the number of the stratification as counted either from the primary or secondary negative pole. I assume here that the tube is of the same width throughout.

The intervals between the different stratifications need not be the same. The interval, for instance, between the negative light and negative end of the first positive stratification is always larger than the interval between two positive stratifications, if the tube is of the same width throughout.

The facts described in the three following paragraphs follow from this statement. I always mean by negative or positive pole secondary as well as primary poles.

30. The limit of the positive light is independent of the position of the positive pole, and therefore also of the distance between the two poles.

31. Shifting the negative pole in the direction of the discharge produces a shifting of all stratifications in the same direction; in cylindrical tubes each stratification moves through the same distance.

If the negative pole is moved towards the positive pole, as many stratifications disappear as were placed in the length through which the negative pole was moved; if the distance between the positive stratifications is constant, which is generally approximately the case, the number of the disappearing stratifications are equal to the number obtained by dividing the length through which the negative pole was moved by the distance between the stratifications. On moving the negative pole away from the positive pole, the same number of stratifications reappear.

32. A movement of the positive pole produces also an appearance or disappearance of stratifications; but in this case the stratifications themselves remain stationary.

If the positive pole approaches the negative pole to a distance smaller than that between the negative pole and the first positive stratification, the positive glow disappears altogether.

33. It follows that tubes may be prepared which do not show any positive light; the negative light is surrounded by the dark space, which reaches to the positive electrode, and which often takes up the larger portion of the tube.

We may have either tubes which show this phenomenon only at one particular pressure, or at all pressures, according as the distance between the electrodes is smaller than that at which a stratification may appear for one pressure only or for all pressures.

34. On exhausting a tube, the stratifications get longer, just as the negative light is known to get longer. At the same time the distance between the stratifications is increased. Both changes seem to go on without limit, and cause the appearances described in the two following paragraphs.

35. With decreasing pressure all stratifications move towards the positive pole, and the stratifications decrease in number, disappearing one by one at the positive pole. If the tube is not sufficiently wide to show stratifications along its whole length, the unstratified light moves bodily towards the positive pole, just as if it were stratified.

36. Finally, tubes may be prepared in which not only the whole positive light has disappeared, but also the dark space, so that only the negative glow remains, which fills the whole tube. This effect is produced at pressures which are the higher the shorter the tube is.

The distance between the stratifications is therefore the magnitude which chiefly determines the appearance of the electric discharge.

37. This magnitude, which was shown to be independent of the length of the tube, varies not only with the pressure, but also very much with the dimensions of the tube. I do not give here a very general law which regulates all these phenomena, as it would necessitate a long discussion of experimental details; the facts may be expressed as follows:—

If all the cross sections of a tube are altered so that the surface of the tube remains similar to itself, the distance between the stratifications increases. The tubes may have any shape whatever, either prismatic, conic, cylindric, or ellipsoidal. For example:—

If conical tubes are cut out of a given cone at different distances from the vertex, the distance between the stratifications is the greater the greater the distance from the vertex.

In cylinders of different widths, the wider they are the greater is the distance between the stratifications.

The first positive stratification is therefore the more distant from the negative pole the wider the cylinder is. This explains an observation of Wüllner*, who, in his "Studies on the Discharge of Induction-Currents in Vacuum-Tubes," says, "Increasing the width of a tube diminishes the positive glow."

38. In conclusion, I may mention the remarkable effect which two surface-elements of two negative poles have on each other, even at a distance of several centimetres. If two pieces of foil, for instance, are used as negative electrodes, the brightness of the light is much increased on the sides of the foil which are turned towards each other; it is decreased on the other side.

The strong diminution in size which the second stratification of the negative glow undergoes at the sides which are turned towards each other is also very striking. This fact may be useful when an increase in the brightness of the negative glow is required, as, for instance, for purposes of spectrum-analysis. A short brass tube $\frac{3}{4}$ centim. wide could be used as negative pole for that purpose.

* Pogg. *Ann.* Jubelband.

XLIX. *On some Dynamical Conditions applicable to* Le Sage's *Theory of Gravitation.* *By* S. Tolver Preston*.

No II.†

1. THE explanation of gravitation has now risen to the rank of one of the foremost problems of modern science; indeed the day for the ascription of occult qualities to matter is now gone, and phenomena, demand an explanation by the reason. The ascription of an occult quality, so far from throwing light upon a phenomenon, only serves to darken it. The effects of gravity (like all other physical effects) being effects of motion, have, like other physical effects, to be explained. A rational explanation has to be given for the motion of approach of two masses. If we were to make an exception of this case, it might be argued that we might make an exception of other cases; and since *all* physical effects are effects of motion, we should thus in principle have nothing to explain at all.

2. The absolute necessity for giving an explanation of gravity being admitted, we may inquire what has hitherto been done in this respect. The *only* theory worthy of serious consideration, or which has stood any test at all, is the theory put forward by Le Sage of Geneva. An immense advance in dynamics has been made since his day. It therefore behoves any one to ask how far the principles put forward by him admit of being improved and modified according to modern advances in dynamics.

3. To any one who has carefully read Le Sage's theory‡, it will be evident that the theory consists mainly in a series of postulates or conditions arbitrarily assumed so as to be adapted to produce the results required. Le Sage assumed (1) the movement of streams of particles coming from an indefinite distance in space and converging towards the visible universe. He even calculates (by a given velocity of motion) the distance those particles would require to have come which produce gravitation, at a remote epoch of 10,000 years (page 22). He therefore calls the particles, from the enormous distance he supposes them to come, "*ultramundane* particles." Next he assumes, quite arbitrarily, that the particles move *uniformly or equally in all directions*, this being necessary in order that the action

* Communicated by the Author.

† The other part may be found in the 'Philosophical Magazine' for September 1877. Certain points are recapitulated in the present paper for completeness. A paper "On the Mode of the Propagation of Sound" (Phil. Mag. June 1877) also bears on the subject.

‡ The theory is given in a work entitled *Deux Traités de Physique Mécanique*, by Pierre Prevost.

of gravity may be equal in all directions. He computes (roughly at about 3,000,000) the number of different directions in which separate streams of particles would require to be moving in order to produce everywhere that sensible uniformity of pressure which is the characteristic of gravity (page 25). It will be noted that these are all assumptions in themselves entirely arbitrary. He next assumes that the mean velocity of the streams of particles is everywhere the *same*, and the density everywhere the *same*.

4. It will be observed that this theory gives no possible idea as to how such a motion of streams of particles among themselves could be kept up, or naturally maintained. Le Sage attempts to evade the difficulty of the particles encountering each other by assuming them to be so small that "not more than one out of every hundred of the particles meets another during several thousands of years." This only removes the difficulty a step further on, without avoiding it. Indeed it may be observed that the theory, in the state in which Le Sage left it, is little more than a series of postulates, some of them almost as unrealizable as gravity itself. This does not detract from a distinct merit in the origination of the theory; for it must be remembered how little dynamical principles were advanced at Le Sage's time, and how few resources he had to draw upon.

5. I have pointed out (Phil. Mag. Sept. 1877) what (whether already observed by others or not) cannot but be regarded as a somewhat startling fact, viz. that no postulates whatever are required for a dynamical theory of gravitation, but that it may be shown that particles of matter in free motion in space must inevitably of themselves arrange their motions so as to produce the effects of gravity—or the special effects of gravity (variation as the square of the distance &c.) must be produced from pure dynamics in the case of a system of particles in free motion in space, without any necessity for postulates as to the character of the motion at all. This follows from the principles which have been investigated in connexion with the modern kinetic theory of gases, of which Le Sage was ignorant. For it has been demonstrated by Professor Maxwell, in connexion with the kinetic theory of gases, that particles of matter in free collision among each other in space will *automatically* arrange their motions so as to move *uniformly in all directions*, i. e. so that an equal number of particles are moving in any two opposite directions (this being the necessary condition for equilibrium of pressure in a gaseous medium*). This cha-

* I may state that I had independently arrived at this same result in a paper "On the Mode of the Propagation of Sound on the Basis of the

racter of motion, it may be observed, is the first important condition required by Le Sage's theory—which condition therefore follows as a rigid dynamical fact, not as an arbitrary postulate, as he made it. This motion of the particles *uniformly or equally towards all directions* is not a mere chance fact, but a rigid adjustment, of such a character that when by any artificial means this mode of motion of the particles is disturbed they will automatically, of themselves, return back to this *regular* form of motion (*i. e.* so that an equal number of particles are moving in all directions). The other conditions put forward as postulates by Le Sage, viz. that the density of the streams of particles should be the *same* in all parts, and the mean velocity the *same* in all parts, are equally necessary results following from the kinetic theory of gases—not, therefore, postulates at all.

6. The only further condition required is that the mean length of path of the particles, before being intercepted by collision with each other, should be great enough to produce the effects of gravity—*i. e.* so that the particles of the medium may act as streams upon masses immersed in the medium, or may stream past two opposed masses, which by their mutual screening or sheltering action produce the observed effects of gravity. The mean length of path of a particle depends (as is known) upon its size. One size of particle is not *à priori* more likely than another. By simply, therefore, making the particles small enough, any mean path, however great, may be attained. We thus observe that all the arbitrary postulates of Le Sage's theory, together with all the effects of gravity, naturally and inevitably follow from the simple admission of the existence of matter in space whose normal state is a state of motion, or the existence of a medium in space constituted according to the kinetic theory of gases. In this way the mode in which the motion of the streams of particles through each other is naturally kept up in a state of dynamical equilibrium, is quite easily explained.

7. Here we do not want an indefinite waste of matter, or an indefinite supply of matter from ultramundane space (as Le Sage imagined) to produce gravity, but gravity is produced by matter or a medium which *as a whole* is stationary, and whose internal motion is kept up and perfectly naturally maintained by the rigid laws of dynamics. The difficulty of the collisions is here completely got over; for the collisions of the particles among each other, so far (as Le Sage supposed)

Kinetic Theory," published in the 'Philosophical Magazine' for June 1877, without being aware at that time of Professor Maxwell's result.

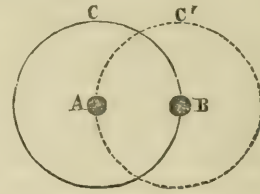
from interfering with the uniformity of their motions, is the very condition which corrects and *maintains* the uniformity of motion in opposition to external disturbing causes. This is the main point which was utterly inexplicable in Le Sage's theory; for it was impossible to see, in the way he put it, how such a motion of streams of particles should be kept up uniformly in all directions, under continual collisions with themselves and with mundane matter. By the application of the principles of the modern kinetic theory of gases to the case, this point is completely solved. As before remarked, it is almost startling that the particular form of motion which the particles themselves automatically keep up should be precisely that one which is required to produce gravity (or an effect varying as the square of the distance &c.),—also that it should make the *density* and *mean velocity* equal in all parts, which is necessary for the effects of gravity*.

8. It is an interesting fact to observe that the distance through which gravity will act will depend on the range through which the streams of particles are comparatively unimpeded, *i. e.* on the mean length of path of the particles. By making, therefore, the mean length of path of the particles less than the average distance of the stars, it would follow that the stars do not gravitate towards each other, which satisfies the condition for the stability of the universe. It is evident (as has been already pointed out by others) that the assumption of all the bodies of the universe gravitating towards each other is quite inconsistent with stability; and to the truly philosophical mind any theory which rendered such an assumption of instability necessary would be in itself improbable. It is only necessary that the mean length of path of the particles be great enough to produce effects of gravity through-

* I have been informed by Professor Tait that a book published in 1818 by Dr. Blair (Regius Professor of Practical Astronomy in the University of Edinburgh) has come under his notice, in which is sketched a theory of gravitation quite similar to that of Le Sage. A later edition of the book, under the title 'Scientific Aphorisms,' was published in 1827. Dr. Blair attempts to account for the motion of the particles being kept up *uniformly in all directions* by assuming them to rebound from the interior of a hollow spherical surface, which is supposed to bound the visible universe. Of course he, like Le Sage, was ignorant of the remarkable fact of the particles themselves automatically arranging their motions so as to move uniformly in all directions, which has been brought to light in the investigations connected with the kinetic theory of gases. The spherical surface is of no use to guide the motions of the particles; for they do this themselves. It may be observed that Fatio and Redeker developed a similar theory to that of Le Sage, to a certain extent. When we thus find several minds arriving at the same result, this forms an additional argument for its truth.

out the greatest range in which we have observed them, which is but an infinitesimal fraction of the distance of the stars *.

9. It may perhaps be well just to sketch here the mode of action of the medium in producing gravity, the manner in which the intensity is made to vary as the *square* of the distance, &c. Let A (in the annexed diagram) represent a molecule or mass; let C represent the bounding surface of an imaginary hollow sphere described about A. Then, since the particles of the medium are moving uniformly in all directions, a number of them will be passing in all directions through the imaginary spherical surface C. Only those particles which are passing (sensibly) along the radii of the spherical surface will strike A; and therefore we need only regard those special particles which radiate towards A. The molecule A being therefore struck equally on all sides, will accordingly remain at rest. But if now we suppose a second molecule to be placed at B, then out of the whole number of particles which are directed towards A, the molecule B will intercept a number which is proportional to the area which B cuts off from the whole spherical area C. The molecule A will therefore now, owing to the sheltering power of B, be struck with a fewer number of particles in the direction B A. The balance of the pressure being thus upset, A will be propelled towards B. The same holds true of B relatively to A (on drawing the imaginary spherical surface C′). The two molecules A and B are therefore propelled towards each other mutually. It now remains to illustrate how the impulsive action varies as the *square* of the distance. It will be at once evident that since the area of a spherical surface is as the square of the radius, therefore, if B



* It may just be noted in connexion with this, that if the above deduction as to the stars not gravitating towards each other be true, those stars which have a proper motion must be moving in *straight lines*.

It is of course evident that all the relations (admirable in their simplicity) existing between the velocity of the particles, the pressure, and density of the medium (or quantity of matter in unit volume), the dimensions, distance, and mean path of the particles, which apply to the kinetic theory of gases, apply equally to the gravific medium,—as also the physical relation existing between the velocity of the particles and the velocity of a wave in a gaseous body, pointed out by me (Phil. Mag. June 1877), the numerical value of which (as determined by Professor Maxwell) was given in the above paper. The assumption is perhaps not unwarranted that it may eventually be possible, by determining the absolute value of some of the above relations, to calculate the mean path, and therefore the range of gravity.

were removed to a double distance, the imaginary spherical surface described through B with A as a centre, would have four times the area; but the area of the molecule B remaining constant, B would therefore only shelter A one fourth the amount it did before; and accordingly A would be impelled towards B with one fourth the force,—the same being true of B relatively to A.

10. It is found that gravity is proportional to mass. It must therefore be assumed that, owing to the porosity of bodies, or open structure of the molecules, the gravific medium (whose particles are extremely minute) can penetrate freely into the interior of bodies, and thus act upon the internal molecules, so that the total effect is proportional (sensibly) to the number of molecules, or gravity is proportional to mass. Of course this could not hold true with an infinite mass; but it is rigidly demonstrable (by a given degree of porosity) that it could hold true with as near a degree of approximation as experience has shown, and even nearer if necessary. Independent physical reasons for inferring this extreme porosity or permeability of matter will be given further on.

11. My main object in this paper is to meet all possible objections which have been or might be urged against this theory, as, if it be true, it ought to stand against all criticism; and if, on the other hand, it be erroneous, the sooner it is demonstrated so the better. It may just be remarked, in the first place, that *in principle* there appears to be no other theory conceivable which at all would satisfy the conditions of gravity. Gravity can be referred to two conceivable causes:—(1) to a motion possessed by the molecules of matter themselves, disturbing the equilibrium of pressure of the surrounding medium; (2) to an independent motion of the medium itself acting upon the molecules. The first of these two conditions appears to be inadmissible; for if gravity were due to a motion of the molecules of matter, then since we can readily modify or interfere with the motion of the molecules of matter (as by heat), we could thereby interfere with gravity. The fact, therefore, that it has been found impossible to interfere with gravity, points to a motion in the external medium (which is beyond our control) as the cause. It would be well to keep this fact in view before lightly regarding Le Sage's theory as a mere *hypothesis*. To the careful observer it will appear to contain rather the essence of a *necessary* fact, from the absence of (in principle) any other conceivable cause; and if the theory can be shown to be a practical one, consistent with admitted mechanical principles, it will have every condition for acceptance. To us it seems that a closer study of the theory only serves to show its

many mechanical beauties and extreme simplicity as a means to an end, satisfactory, not only in the absence of any other conceivable cause, but as affording a perfectly rational conception to the mind of the processes by which the effects are brought about.

12. The most difficult thing perhaps *at first sight* is to conceive the great permeability or porosity of matter necessary to this theory. It may be perhaps just noted in passing, that most *truths* are strange *at first sight*, or else it would be competent for any one to arrive at them. I think it may be shown that this open structure of matter is a thing in itself probable, and also distinctly warranted on independent grounds. In architectural and engineering structure generally we do not observe a solid block formation, if I may so express it, but that *open* structure which is essential to elasticity and strength. So in molecular architecture, we may not expect to find a mass a solid block, but of open structure, though we naturally cannot *see* the interstices. Again, the perfectly free passage of light or the waves of æther through a piece of glass, or a wave of obscure heat through a block of rock-salt, also of the magnetic disturbance through all matter, would by itself prove the extremely open structure of matter. There is therefore no difficulty in admitting the openness of structure of matter essential to the dynamical theory of gravitation, as this is in itself a natural thing, pointed to by other facts*.

13. The next difficulty is one pointed out by Professor Maxwell in a notice of Le Sage's theory (*Encycl. Brit.* 1875, page 46, under the word "Atom"). The argument there is that, in view of the demonstrated fact that particles of matter in collision with each other tend to acquire the *same* kinetic energy, therefore the kinetic energy of a molecule of ordinary matter would ultimately tend to become equal to that of a gravific particle, and that therefore it would appear that the continual impacts of the particles of the gravific medium would necessarily raise matter to an enormous temperature, as the velocity of the gravific particles must of necessity be assumed extremely high. This objection would seem to have considerable weight; but I think it admits of being surmounted on taking certain facts into consideration. It will be admitted that, in order to produce gravity, it is only neces-

* It may be observed that since, by the rejection of the theory of "action at a distance," *all* motions developed in matter must inevitably be referred to external media, so therefore, in order that matter may be worked (so to express it) by external media, it must have an open structure—as, in analogy, a steam-engine must have an internal open structure in order that the steam may get at the working parts.

sary that not less than a certain *total* of energy should be contained in a given volume of the gravific medium, not that thereby the energy of *each* particle should necessarily be great. The energy of each particle (whose sum produces a given total of energy) would evidently depend on the number of particles in unit volume. Professor Maxwell assumes that it is "tolerably certain that N, the number of (gravific) corpuscles which are at any one time within unit of volume, is small compared with the value of N for the molecules of ordinary bodies." Now we may ask, Is this *certain* or necessary? for the whole hinges upon this. If, on the contrary, the number of gravific particles in unit volume were not restricted, then by adding to the number of particles, and thus subdividing the total energy among them, the energy of each particle might be made indefinitely small. It might possibly be thought that such a number of particles would be inconsistent with a long free path. But if the subject be considered, it will be observed that a free path of given adequate length may be obtained with an indefinite number of particles, provided the particles be minute—or that, no consequence how numerous the particles (and therefore how small the energy of each), an adequate mean path can be got by reducing their size, their velocity being augmented so as to keep the energy in unit of volume constant. This high velocity of the particles may be shown on other grounds to be a likely condition; for by this means the whole medium is rendered completely impalpable, or its presence vanishes from the senses—the medium opposing no measurable resistance to the passage of bodies through it. Accordingly, as by a given amount of energy in unit volume the energy of each particle is inversely as their number, so by multiplying the particles the energy of each may be made indefinitely small; and therefore the energy transferred to the molecules of matter would be made indefinitely small, or there would be no measurable rise of temperature at all. This, I submit, removes the difficulty in question.

14. It was pointed out by Le Sage that, in order to explain gravity, it is necessary to assume that the gravific particles rebound from the molecules of matter at a less velocity than they strike. Since, after the average kinetic energy of a molecule of matter has become at least equal to that of a gravific particle, no further transference of energy can take place from the gravific medium to matter (*i. e.* of course in the case of matter at rest), it is necessary therefore to explain the diminished velocity of rebound of the gravific particles. Sir William Thomson (Phil. Mag. May 1873) has pointed out that this may be a natural consequence of a difference of elastic rigi-

dity between the gravific particles and the molecules of matter. There may possibly be some who may be inclined to think that this explanation was somewhat forced, or was warranted only as explaining that special case, without being independently likely. I think that, on considering the subject, it will be found that the explanation is in itself highly probable on independent grounds. Where do we find substances in nature whose elastic rigidity is the *same*. It would be in the highest degree unlikely that portions of matter differing so vastly from each other in dimensions as a molecule and a gravific particle should have the *same* elastic rigidity. If the elastic rigidity be not the same, it is a strict dynamical fact, not a supposition, that the energy of the particle after its rebound from a molecule, though the same in amount, will not be the same in *kind* as before; but if the elastic rigidity of the large molecule be greater than that of the minute particle, a part of the translatory motion of the particle will be shivered into vibratory motion at the encounter; and therefore the particle will rebound with a less translatory motion, the deficiency of translatory motion representing the amount converted into vibratory motion at the encounter. It is just as if a tuning-fork, a flexible ring, or any pliable elastic object whatever, were thrown against a hard body (say the hard surface of an anvil), when the body will rebound at a less translatory motion than it struck, the deficiency of translatory motion being compensated for by an accession of vibratory motion. So with a gravific particle striking a molecule of matter; for mere size makes no difference in the principle. It is therefore not an unnatural thing (but highly probable on independent grounds) that the gravific particles should have their velocities changed at impact against the molecules of matter. The energy of the particle remains unaltered by the impact; only the distribution of the energy in the particle is changed.

15. The next question is, Do the particles which have thus lost translatory motion and acquired an accession of vibratory motion, recover their normal proportion of translatory motion to vibratory motion again? It has been pointed out by Sir William Thomson that this must be the case. For it has been demonstrated by Professor Clausius, in connexion with the kinetic theory of gases, that, in the case of a system of particles in free collision among themselves, the relation of the translatory motion to the vibratory motion tends to assume a constant value, so that when this relation is disturbed in any way it is again restored. So, therefore, when the relation of the translatory motion to the vibratory motion of the gravific particles is disturbed by collison with the molecules of matter, this re-

lation is again restored to its normal value by the collisions of the particles among themselves. This, it may be observed, is therefore a rigid dynamical fact, not an hypothesis.

16. There is therefore no expenditure of energy or work whatever in the maintenance of gravity, since the total amount of energy in the particle is unaltered by collision. Also no supply of energy to the gravific particles is required, since a state of motion is as natural as a state of rest. Further, no supply or waste of matter is required for the maintenance of gravity. Le Sage imagined that a continual supply of matter from ultramundane space was necessary. He endeavours to get over this incongruous idea by making the excuse "that nature makes frequently such waste" (page 108). This is evidently no satisfactory excuse at all; in fact Le Sage, with the limited knowledge of his day, naturally could not get over the difficulty of the collisions, or could not form an idea of the conditions of equilibrium of streams of particles of matter moving in the way he assigned. With our modern knowledge we may deduce that the conditions of equilibrium of such streams of particles are of a perfectly definite character, so as to produce gravity as an inevitable fact. The gravific medium, therefore, within the bounds of the visible universe is *as a whole* at rest; and no supply of matter whatever is required. The medium producing gravity is simply a medium constituted as a gas according to the kinetic theory—but quite exceptional in character as regards the extreme minuteness of its particles, their extremely high velocity, and long mean path, the high velocity rendering the medium completely impalpable, or its presence imperceptible to the senses. It is evident that the presence of such a medium could be only rendered directly palpable to the senses by the *resistance* attendant on the motion of bodies in it. Now it is a known dynamical fact that this resistance diminishes as the velocity of the particles of the medium increases; hence with a given velocity no resistance whatever will be felt, and therefore the presence of the medium must elude detection. These deductions are therefore in perfect harmony with the facts. The mean length of path of the particles of the medium, though great compared with that in the case of ordinary gases, may be considered small in proportion for a gaseous medium that pervades the area of the visible universe.

17. It would be a wrong idea to imagine that, because the particles of the gravific medium are relatively very close compared with the molecules of ordinary substances, therefore the quantity of matter forming the gravific medium must be relatively great. It is a mathematical fact that the

total quantity of matter contained in (say a cubic mile) of the medium might be indefinitely small, and yet the particles indefinitely close together, provided the particles are very minute. By a given velocity of the particles of a medium, the uniformity or steadiness of the pressure exerted against matter evidently does not depend on the size of the particles, but on their closeness (which determines the rapidity of succession of the collisions against matter). By a given proximity of particles, therefore, no consequence how minute they may be (and therefore how small the quantity of matter composing the medium), the pressure will remain equally steady. It follows, therefore, that a medium may produce all the uniformity of pressure due to the flow of a continuous fluid, and yet the quantity of matter composing the medium may be indefinitely small. Owing to the frequency of the collisions against matter, due to the close proximity of the particles of the gravific medium and their high velocity, the pressure exerted by the medium is so even and regular as to be imperceptible to the senses, excepting in the effect "gravity." The pressure termed "gravity" due to the motion of the particles of the gravific medium is no more difficult of realization than the pressure of the air due to the motion of its molecules. To get a true idea of the nature of the gravific medium, the conception of extreme closeness of arrangement of the particles, combined with extreme rarity of the medium, must be kept in view. It is easily conceivable, for example, that the particles of a cubic foot of the medium may be in very much closer proximity than the molecules of a cubic foot of lead (from centre to centre), and yet the total quantity of matter contained in a cubic foot of the medium may be less than that contained in a single molecule of lead.

18. The agent producing gravity must therefore not in any way be looked at (as one might possibly be liable to do at first sight) as representing a prodigious quantity of streams of gross matter flying about, but simply as the quiet imperceptible motion of a relatively very small quantity of excessively finely subdivided matter which produces a perfectly uniform pressure, the energy of each particle by itself being totally imperceptible; or only the resultant effect or pressure is noticed, the inexorable motion of the particles (and the resultant effect "gravity") being as incapable of being interfered with as the conservation of energy itself. Surely no more rigid, constant and unalterable cause could be conceived of than that of the normal motion of the particles of a medium among themselves, which, by an inevitable automatic adjustment arrange their motions so as to produce the effects of gravity. "Gra-

vity" is distinguished by its unalterability under the influence of heat, and general constancy under all conditions. Could a more constant cause be imagined than the above? and could a more simple one be desired? or could any other means of satisfying all the conditions of the problem be conceived of? If simplicity be a mechanical recommendation, the simplicity of the above conditions will recommend themselves. We say simplicity; for surely we have the *ne plus ultra* of simplicity, when no postulates at all are required, but the total sum of effects may be said simply to evolve themselves out of pure dynamics.

London, October 1877.

L. *On Unitation.*—VII. *Practical Remarks thereon, together with Examples. By* W. H. Walenn, *Mem. Phys. Soc.**

[Continued from vol. i. p. 549.]

24. In considering the nature of a unitate and of the operation of unitation, the method of thought is new to mathematical minds, and does not readily fall in with the routine of ordinary mathematical work; for this reason it is necessary to treat the matter somewhat in detail. The whole subject is fundamental, and is characterized by constant reference to first principles of the simplest kind. It is its very simplicity that creates a difficulty in the facile apprehension of a unitate as a function, and of unitation as an operation. From what has been written it will be perceived, upon examination, that it must by no means be confounded with the remainder to a division*. The denomination of the remainder to a division is determined by the denomination of the last figure of the quotient; but a unitate, in its strictest sense, is an integer; for it is one of a series of integral values (each member of which is made up of units), the series being determined by the base of the system of unitates, and extending from 1 or unity to the numerical value of the base itself.

Thus, in dividing a given number by 20, to find the remainder to that division, if the number has a decimal portion, the remainder will be less than unity†. For instance, the division $\frac{40{\cdot}123}{20}$ gives for remainder ·003; but the unitate of the number 40·123 to the base 20 is 3, since it must be one of the numbers 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20. The name unitation is given to the operation to note this distinction in the most marked manner possible. This peculiarity is pointed out in the Philosophical Magazine

* Phil. Mag. [V.] vol. ii. p. 348. † Ibid. p. 345.

for November 1868, p. 346, for December (Supplement) 1875, pp. 522, 523, 524, and for November 1876, pp. 345–350 inclusive. In other words, the remainder to a division is dependent for its value upon the quotient, and is a function of an expression containing the quotient; whereas a unitate is quite independent of the quotient, and is a function of an expression that does not contain the quotient. The expression of which it is the function contains only the number to be unitated and the base of the unitation; the way in which the base affects the unitate is as the determinator of the extent of a series of integral values, commencing with unity and finishing with the base itself. The unitate may therefore be said to express the place of its corresponding number in a recurring series whose period is the base of the system of unitation.

25. The numeration of unitation is therefore limited by the base, and, with certain exceptions, always consists of *integer* numbers ranging between unity and the base. The exceptions arise from an extension of the meaning of the word unitate, or rather from including in the list of unitates numbers not originally comprehended in the definition, but which, for certain purposes, fulfil their conditions,—just as, by analogy, the decimal 1·414213.... is properly made to do duty for $\sqrt{2}$; whereas by the construction of numbers, which makes all numbers functions of unity, $\sqrt{2}$ is not a function of unity, but is incommensurable therewith. The exceptions occur in the case of fractional unitates, as shown in the Philosophical Magazine for July 1873, p. 38 *et seq.*, and in other cases. For instance, strictly speaking, there is no unitate (to the base 9) of $\frac{1}{3}$, nor any number whose unitate is $\frac{1}{3}$. Taking the unitate of $\frac{1}{3}$ and of $U_9^{-1}\left(\frac{1}{3}\right)$ as equal to $\frac{1}{3}$ has, however, an advantage over the decimal equivalent of a surd quantity, inasmuch as it completely fulfils the conditions of the principles of unitation (see Phil. Mag. July 1873, p. 40); whereas the interminable decimal 1·414213.... can only approximate to the result, although the degree of approximation is practically unlimited, or limited only by the labour of calculation.

26. If the application of the theory of functions to unitation had not yielded such definite and such original results, and if the interpretation of symbols had not been brought to bear upon the whole subject with especial rigidity and care, unitation would have been merely a name for something that existed already, namely the obtaining remainders to divisors; but the

application of the theory of functions shows that each unitate, of the normal kind, must of necessity be an integer; the interpretation of symbols points out that the symbol $U_\delta x$ is a perfect representation of "the unitate of the number x to the base δ," and that therefore $U_\delta^{-1}.x$ is the representation of the phrase, "any one of the series of numbers whose unitate, to the base δ, is x."

27. Many advantages are gained by the fixedness of whole numbers, as in unitation, over the variability of the denomination and meaning of remainders to division. The first instance is treated of in the Philosophical Magazine for July 1873, p. 40. By no kind of division could $\frac{1}{7}$, or $\cdot\dot{1}42857\dot{}$, have been divided by 9 so as to give 4 as a remainder; yet, regarded as a number which has the same unitate to the base 9 as $\frac{1}{7+9}=\frac{1}{16}$, the result is easily arrived at. Other instances of this occur, especially when δ, the base of the system of unitation, is a prime number; for in $U_\delta x^{-n}$, when δ is a prime number, the only fractional unitate is when x is some multiple of δ. Consequently the intractable recurring decimals $\frac{1}{3}(=\cdot\dot{3})$, $\frac{1}{6}(=\cdot1\dot{6})$ and $\frac{1}{9}(=\cdot\dot{1})$, in the series of unitates represented by $U_{11}x^{-1}$, are respectively symbolized and finited as follows:—

$$U_{11}\frac{1}{3}=U_{11}\frac{1}{25}=U_{11}(\cdot04)=4,$$

$$U_{11}\frac{1}{6}=U_{11}\frac{1}{50}=U_{11}(\cdot02)=2,$$

$$U_{11}\frac{1}{9}=U_{11}\frac{1}{20}=U_{11}(\cdot05)=5.$$

Another instance of simple results being substituted for interminable or incommensurable ones is alluded to in the Philosophical Magazine for August 1875, pp. 119, 120, in which $U_{11}\surd3=5$, and $U_{11}\surd5=4$. The above instances all refer to the simplification which occurs in the numeration of unitates, by adopting the definition for them in its rigid integrity and fearlessly working out the results.

28. The ordinary formula under which numbers are placed, when their properties are to be investigated by algebraical means, may be stated as

$$a_0+a_1r+a_2r^2+a_3r^3+\ldots.+a_{n-2}r^{n-2}+a_{n-1}r^{n-1}.$$

In this formula r is the radix of notation in which the number is expressed, a_0, a_1, a_2, a_3, &c. are the digits that compose the number, each being less than r; and there are n digits. When the radix is 10, this formula becomes

$$a_0+10a_1+10^2a_2+10^3a_3+\ldots+10^{n-2}a_{n-2}+10^{n-1}a_{n-1}.$$

The mathematical mind has been so much imbued with this formula, or with formulæ that are exactly its counterparts, that any deviation from the recognized method of working demands the giving of such substantial reasons as shall assure the reader of the advisability of the alteration.

It is conceded by all, that the form or method of arrangement of a formula must be that which is best suited to the object in view; for instance, in the theory of equations the general formula is always arranged in descending powers of x, the highest power being towards the left hand. The very life of unitation depends upon the treatment of it in a perfectly appropriate and orderly manner, taking into account analogy and exactness of form to express the general idea that is intended. Every number, regarded as a function of its radix, must have its highest power to the left hand.

Again, in the ordinary formula, nothing is gained by having the series of digits marked by a_0 at the beginning; on the contrary, by this arrangement the general term does not express the number of digits readily. On these grounds the formula is taken here as

$$a_nr^{n-1}+a_{n-1}r^{n-2}+\ldots+a_3r^2+a_2r+a_1;$$

or if $r=10$,

$$10^{n-1}a_n+10^{n-2}a_{n-1}+\ldots+10^2a_3+10a_2+a_1.$$

Thus arranged, the formula is a picture of the number in algebraical language; this will be seen to be an important point in the method of working with the formula for the purposes of research and investigation.

74 Brecknock Road, N.,
October 5, 1877.

Addendum.—Since writing the above, the Report of the British Association for 1876 has come into the hands of the author. The statement in the Transactions of the Sections is as follows:—"The author referred to a series of papers of his on unitation recently published in the 'Philosophical Magazine,' and to some remarks published in the British-Association volume for 1870. If x divided by δ leave remainder y, then the author calls y the unitate of x to the base δ, and writes $U_\delta x=y$.

The results of 'unitation' may be conveniently applied to the verification of many numerical operations. The method of unitation is practically equivalent to the theory of congruencies; viz. the equation $U_\delta x = y$ would be written $x \equiv y \pmod{\delta}$; and many of the results are identical with those given by Gauss." This statement is different from that contained in the paper (see Phil. Mag. November 1876, p. 345 *et seq.*), and it has no warranty from the author. The original title of the paper was "On a new Mathematical Function;" in compliance with a simple request, and considering that the starting-point of the paper was division-remainders, the author permitted the title to be altered to "On Division-remainders in Arithmetic." The statement in the 'Report' misinterprets the meaning of the author—inasmuch as the paper was not intended to identify the function $U_\delta x = y$ with the statement "x divided by δ leaves remainder y," but to point out the great distinction between the remainders in arithmetic and the periodic and discontinuous function $U_\delta x$. The symbol $x \equiv y \pmod{\delta}$ does not presuppose any function, but simply expresses a statement which has for its basis the division-remainders as obtained by actual division, and therefore has no part with unitation.

October 8, 1877.

LI. *On some Points connected with the Chemical Constituents of the Solar System.* *By* J. H. Gladstone, *Ph.D., F.R.S., Pres. C.S.**

In a recent course of lectures on the Chemistry of the Heavenly Bodies, various considerations occurred to me, which are not to be found in the ordinary treatises on the subject. I have since found that Mr. Norman Lockyer's recent lecture at Manchester deals with some of these; but the following are, as far as I am aware, novel, and may be worthy of record as a contribution to a line of thought which is being at present considerably developed.

I. The discoveries by means of the spectroscope, and the general advance of knowledge of the heavenly bodies, have tended greatly to confirm the nebular theory of the creation of worlds. Assuming a hot nebulous mass made up of many different chemical elements gradually condensing towards a centre, the question arises, How will these elements be distributed? This would depend upon two different circumstances

* Communicated by the Author, having been read at the British Association, August 1877.

of a physical nature. (1) Of course the cooling of such a nebulous mass must take place from its outer portion, giving rise to a distribution of temperature greatest at the centre and gradually decreasing towards the circumference. One of the results of this would be that the least volatile constituents near the circumference would condense and sink towards the centre of gravity, forming eventually the liquid or solid nucleus, while the most volatile would still extend to the outermost portions of the nebula; and the rest would arrange themselves in the order of their volatility, condensing into cloud at various distances from the intensely heated centre. (2) But there is another law regulating the arrangement of the gases, which has been pointed out and mathematically proved in a paper communicated to the Royal Society by Mr. G. Johnstone Stoney as far back as May 1867*. He concludes it "to be a necessary consequence of the molecular constitution of gases that in such an atmosphere, decreasing in temperature from within outwards, the various constituent gases are not everywhere equally mixed, but that in the upper regions those that have the lightest molecules rise the furthest, so that the gases overlap one another in the order of the masses of their molecules." We may therefore expect to find the chemical constituents arranging themselves according to their molecular masses so long as they retain their gaseity, and also according to their volatility when condensation has ensued. In either case, however, the separation between the constituents would be far from perfect. The lower stratum of the gaseous envelope will, of course, consist of all the gases diffused together; and while the lighter gases outreach the heavier ones, still the molecules of a heavier gas, shooting about in all directions, will often approach the outer limits of a lighter one. Every one also who has performed a fractional distillation knows how difficult, or rather impossible, it is to separate entirely one body from another by means of the difference in their boiling-points. Now this exactly represents what we actually find in the sun itself. Stretching far beyond its luminous sphere there is an enormous atmosphere of hydrogen, which is by far the lightest of all the gases, and at the same time the least condensable of those which have been recognized in the sun. Far into this atmosphere of hydrogen rise small quantities of sodium and magnesium, both volatile metals, and both giving vapours of exceptional lightness. Lower down we find in large quantities the vapour of iron, certainly a less volatile metal, and

* Proceedings of the Royal Society of London, vol. xvi. p. 25, and vol. xvii. p. 1.

having a greater molecular weight. This is accompanied by other metallic vapours of a similar degree of lightness, which probably condense to form that region of cloud which constitutes the glowing surface that we behold. The spectroscope has shown the absence in the solar atmosphere of mercury, tellurium, bismuth, and antimony, bodies of high molecular weight, which have been detected in Aldebaran—and, indeed, of all the metals of high atomic weight, except perhaps barium and traces of lead. At the same time we find no indication of any of the very infusible metals, such as platinum or gold. As to the centre of the sun itself, we are of course perfectly ignorant of its chemical constitution.

II. Let us now suppose the whole solar system to have been a great revolving nebula condensing to the central sun, and forming from its outer portion such globes as the planets and their satellites, or such accumulations of smaller particles as the comets, meteorites, the group of asteroids, or the rings of Saturn. How may we expect to find these bodies constituted? Clearly we may expect to find that they consist principally of those elementary substances which give the lightest or the least condensable vapours, while at the same time we may expect them to contain smaller quantities of the less volatile and of the heavier ones. Now the earth, though it is one of the planets nearest the sun, must still be regarded as formed from the external part of the great nebula, when we bear in mind the immense mass of the central sun itself. It became of interest to see whether the relative quantities of the known chemical elements in the earth was in conformity with this hypothesis. I asked two of my assistants to draw out a list of the elements, dividing them according to their abundance or otherwise on the surface of the globe. I did not construct this Table myself, lest in any instances my judgment should be warped by the theory which it was intended to test. The following is the Table which they drew up:—

Elements and Vapour-densities.

Non-metallic Elements.

Plentiful.		Not plentiful.	
Oxygen	16	Phosphorus	62
Silicon	28·5	Fluorine	19
Carbon	12	Bromine	80
Hydrogen	1	Boron	11
Sulphur	32	Iodine	127
Chlorine	35·5	Selenium	79
Nitrogen	14		
Average	19·8	Average	63

Metals.

Plentiful.		Rare.		Very rare.	
Aluminium	27·5	Cadmium	56	Platinum	197·4
Calcium	40	Cobalt	58·8	Palladium	106·5
Sodium	23	Bismuth	208	Iridium	198
Magnesium	24	Tungsten	184	Osmium	199
Potassium	39	Gold	196·7	Rhodium	104
Iron	56	Strontium	87·5	Ruthenium	104
Manganese	55	Uranium	120	Lithium	7
Average	37·8	Molybdenum	92	Thallium	204
		Glucinum	14	Vanadium	137
Common.		Titanium	50	Cerium	92
Barium	137	Average	106·7	Lanthanum	92
Zinc	32·5			Didymium	96
Lead	207			Yttrium	68
Arsenic	150			Thorium	231·5
Copper	63·5			Niobium	97·6
Antimony	122			Cæsium	133
Silver	108			Rubidium	85
Tin	118			Indium	74
Chromium	52·5			Tantalum	137·5
Mercury	100			Tellurium	128
Nickel	58·8			Zirconium	90
Average	104·5			Average	122·9

Note.—The numbers represent the atomic weights. It is very possible that the vapour-densities of many of the metals may really be represented by these numbers divided by two, as we know it to be in the case of zinc and others. If this be so, it will not affect the general conclusions.

It will be seen that the average density of those non-metallic elements which are plentiful is 19·8, against 63·0 as the density of the rarer ones. This contrast is still more striking in regard to the metals:—those in the list headed "plentiful" having invariably low vapour-densities, with the average of 37·8; those denominated "common" being nearly always higher, with the average of 104·5; those denominated "rare" averaging 106·7; while the very rare metals have almost invariably high atomic weights, giving the higher average of 122·9. This classification, however, scarcely represents the whole truth, especially in regard to the metals; for as far as we are acquainted with the constituents of the earth, the first six or seven metals are incomparably more abundant than the remainder, while most of the heaviest metals exist but in merest traces. It may also be remarked that not one of the very rare metals is sufficiently volatile for its vapour-density to have been taken. This is quite in accordance with theory, showing that all those elements of which the great mass of the earth is composed are of low density when in the gaseous condition, and that they are mixed with much smaller quantities of bodies which as a rule give heavier and more condensable vapours.

III. The meteoric stones which fall to the earth from interplanetary spaces show this preponderance of the lighter elements still more strikingly. We have the advantage in their case of knowing what is in the interior as well as on the surface, which we do not know of our own globe; but, on the other hand, we know little or nothing of the atmosphere which, by analogy with the other heavenly bodies, we may suppose to surround each meteoric mass before it mixes with our own air. The various known constituents may be classified as follows :—

Elements of the Meteorites.

Plentiful.	Common.	Rare.
Iron.	Carbon.	Vanadium.
Magnesium.	Phosphorus.	Titanium.
Calcium.	Copper.	Tin.
Silicon.	Sodium.	Potassium.
Oxygen.	Cobalt.	Lithium.
Sulphur.	Manganese.	Chlorine.
Nickel.	Hydrogen.	
Chromium.		
Aluminium.		

IV. While the above tables give a general result which is unmistakably in accordance with the deductions of theory, there are evident exceptions in detail. Thus bismuth, which has nearly the heaviest of all vapours, is by no means the rarest constituent of the earth; but then it must also be remembered that it is one of the most volatile metals, and thus would remain in the atmosphere. On the other hand, glucinum, with the atomic weight of only 14, is amongst the rare metals; and lithium, the lightest of all, being only 7, is very small in quantity upon the surface of the earth. Lead, again, with the atomic weight 207, is common. A very natural way of accounting for such exceptions is to suppose that in the original nebula there was but a comparatively small quantity of glucinum and lithium, and a very large quantity of lead; for of course there is no reason to suppose that the nebulous mass was composed of 60 or 70 elements in equal quantities. There is another circumstance which may be expected to interfere with the universality of this rule: compound bodies differ both in volatility and density from the elements from which they are formed, and often without any reference to the mean of their respective quantities. Thus, to take the most familiar instance—water. Oxygen and hydrogen are gases which we have never succeeded in liquefying by any degree of cold or pressure; but the vapour of their compound

is condensable at 100° C. Again, the density of a mixture of two volumes of hydrogen and one of oxygen is 6; but when these gases are combined together, the density becomes 9. Thus, again, carbon is itself very difficult to volatilize; but its compounds with oxygen, or hydrogen, or sulphur, or chlorine, or nitrogen, are gaseous at the ordinary temperature or a little above it. Now it is certain that in the great nebulous mass the force of chemical affinity must be at work in a variety of ways; and the distance of an element from the centre of gravity or heat will depend in no small degree upon the substance with which it is combined; nor does the chemistry of the minerals which constitute the surface of our globe afford much clue to the chemistry of an incandescent nebulous mass. We may learn more from the meteorites, as they were evidently formed at a very high temperature; for they usually consist of rounded masses of siliceous minerals imbedded in a matrix of iron, which has all the appearance of having been soft at the time of their envelopment. Now, although no element has yet been found in the meteorites which does not exist in the earth*, the arrangement of the elements is exceedingly different. Thus we find sulphur and iron combined in the form of a protosulphide (FeS), and other minerals having constitutions which are unknown among those of our globe. We are not free, therefore, to conclude, as Mr. Stoney is disposed to do, that the vapour of barium must have a density little, if at all, heavier than that of iron, since there may be light or volatile compounds of barium with which at present we are not familiar.

V. The heads of comets have been found to be self-luminous, and to emit bands which are usually referred to carbon. The theory has indeed been maintained by some of our most eminent physicists, that the minute bodies of which we have reason to believe comets are composed, consist in a great measure of carbon, and that in rapidly revolving round the head these particles come into collision, with the production of sufficient heat to volatilize the carbon. In fact, the theory maintains that it is not the twinkling stars which shine like diamonds in the sky, but that it is the heads of comets, which are composed

* The meteorites would appear to be a likely field for the discovery of new elements. They will probably exist in small quantities, but recognizable by the spectroscope: indeed it would seem by no means improbable that a diligent search among the residues of meteoric stones after the removal of iron, silicon, magnesium, &c. would reveal substances which would emit rays answering to some of the dark lines of the solar or stellar spectra at present unrecognized. I commend this to the consideration of any young spectroscopist.

of such diamonds. Some corroboration of this theory is to be found in the fact that some meteors contain carbon in the form of graphite; and the connexion between meteoric streams and comets seems to be established. It occurred to me to examine whether the volatilized carbon between the points of an electric light gave out this band spectrum. I found it difficult, though not impossible, by the aid of Mr. Ladd, to throw this light upon the screen without the overpowering flood of light from the white-hot points themselves. A more convenient way of examining it was to throw the image of the charcoal points upon the screen in the usual manner, to place my eye in the intermediate blue, and look at the source of light with a direct-vision spectroscope. I thus found that with large battery-power, and the points far removed from one another, there appeared occasionally a band spectrum, but that generally it burst forth as a multiplicity of bright lines. When, however, the spark was made about as feeble as possible, there appeared pretty constantly the three bands closely resembling those observed in carbon compounds and the heads of comets; and a measurement of the brightest portion, the least-refrangible edge of the middle band, confirmed my belief in their identity*. While, however, it is possible that the light of the heads of comets is due to pure vapour of carbon, there seems to me to be a very serious difficulty in theory. The luminous gas in falling back again to the tail would condense into drops of liquid or solid carbon, which at their first formation must necessarily pour forth a flood of rays of every refrangibility; but this is not the case. It seems to me more probable that the material shining in the heads of comets is of the nature of carbonic oxide, or of those hydrocarbons which we know are occluded in many of the iron meteorites, and which could be easily driven out by any heat, even if they do not form a part of their atmosphere under ordinary circumstances.

We thus see that the deductions drawn from the theory that the solar system was once a great nebulous mass, are borne out by the chemical phenomena accessible to us; and this of course affords another argument in favour of the nebular theory itself.

* After reading my paper, I learnt that Captain Abney had previously made similar observations with the spark of the magneto-electric light.

LII. *Notices respecting New Books.*

A Treatise on Statics, containing some of the fundamental propositions in Electrostatics. By GEORGE M. MINCHIN, *M.A., Senior Moderator in Mathematics and Natural Philosophy, Trinity College, Dublin, and Professor of Applied Mathematics in the Royal Indian Engineering College, Cooper's Hill.* London: Longmans, Green, and Co. 1877. (Crown 8vo, pp. 450.)

THIS work contains all those parts of Statics which are commonly read by students. It is found, we believe, that comparatively few continue their inquiries into the parts of the subject that are here omitted—such as the Equilibrium of Structures and Machinery, and that of Elastic Solids.

The work is divided into fourteen Chapters, of which the first eight are much more elementary than the last six. These eight chapters contain a very full discussion of the composition and resolution and of the equilibrium of forces acting in one plane on a point or on a rigid body. Each of these subdivisions is fully treated. *E. g.* distinct chapters are devoted to questions in which surfaces of contact are supposed to be smooth, and to questions in which they are supposed to be rough; a distinct section is allotted to a discussion of the principle of virtual velocities, or (as Mr. Minchin prefers to call it) the principle of virtual work, in the case in which the forces act on a point, and another section to the case in which they act on a system of two connected points. These two sections form one chapter; a second chapter is devoted to the application of the principle to the case in which the forces act in one plane on a rigid body.

The last six chapters are, as already stated, of a less elementary character than the first eight. They treat, successively, of the equilibrium of a body under the action of any forces, of the determination of centres of gravity, of the application of the principle of virtual work to any system of bodies, of the equilibrium of flexible strings, of simple machines, and of attractions. There is no need for dwelling at length on this list of contents; but it may be noted that several kinematical theorems relating to the displacement of rigidly connected points are given in the chapters treating of virtual work, and that the question of the stability or instability of equilibrium is discussed more fully than is usual in works of about the same scope as the one before us. The chapter on Attractions consists of three sections: in the first the properties of the Potential are investigated and applied to various elementary questions of attractions; in the second the attraction of the Ellipsoid is treated; and in the third, on "superficial distributions," Green's Equation is proved, and the subject of Electrical Images briefly noticed.

The whole of the work—but particularly the first eight chapters—is illustrated by very numerous examples, many of which are fully and many others partially worked out. They are a very valuable part of the work, and the more so as they are made to illus-

trate various methods of solution. There can be little doubt that most students only obtain a firm hold of the principles of Mechanics gradually, by applying them to particular cases.

The printing, form, and binding of the volume are such as to suggest that it is designed as a companion to Mr. Williamson's Treatises on the Differential and Integral Calculus, which have been recently noticed in our pages. We cannot perhaps better express our sense of its merits than by saying that it is well fitted for the position it appears to be designed to fill.

An Elementary Treatise on Musical Intervals and Temperament, with an account of an Enharmonic Harmonium exhibited in the Loan Collection of Scientific Instruments, South Kensington, 1876; *also of an Enharmonic Organ exhibited to the Musical Association of London, May* 1875. *By* R. H. M. Bosanquet, *Fellow of St. John's College, Oxford.* London: Macmillan and Co. 1876. (8vo. Pp. xx and 94.)

Dr. Stainer, in the course of a work on "Harmony founded on the Tempered Scale," used the following words:—"When musical mathematicians shall have agreed amongst themselves upon the exact number of divisions necessary in the octave; when mechanists shall have invented instruments upon which the new scale can be played; when practical musicians shall have framed a system of notation which shall point out to the performer the ratio of the note he is to sound to its generator; when genius shall have used all this new material to the glory of art—then it will be time enough to found a Theory of Harmony on a mathematical basis." Mr. Bosanquet, who quotes this passage (p. xi), seems to have regarded it as a challenge, to which the book before us is in some sort an answer. The main points on which the answer turns he states as follows:—"The theory of the division of the octave has now been completely studied; a generalized key-board has been invented and constructed, upon which all the new systems can be played; a notation has been framed by which, in systems of perfect and approximately perfect fifths and thirds, the exact notes can be indicated; and it has been shown that other systems require no new notation. . . . . The new material may be therefore said to be ready" (p. xi). In explanation of these points we hope the following brief statement will be sufficient, though far from complete. The division of the octave, on which the principal stress is laid, and to which our statement must be limited, is into 53 equal intervals. This is called the system of 53; and in it 31 intervals give a very nearly perfect fifth. In fact, if the interval of an octave be taken as unity, the perfect fifth is 0·58496, the approximate fifth in the system of 53 is 0·58491, while in equal temperament it is 0·58333. The (major) third in the system of 53 is also a close approximation to the perfect third, at all events much closer than the equal-temperament third—the numerical values of the intervals being respectively 0·32193, 0·32075, and 0·33333. Another important point is the following: by tuning up seven fifths and down four octaves, and by tuning down five fifths and up three octaves, two semitones are obtained,

called the seven-fifth and five-fifth semitones respectively—the former consisting (approximately) of 5, and the latter of 4 intervals; and it is easily shown that five of the former and seven of the latter make up an exact octave*.

The facts now recited serve as a basis for a notation which will indicate all the 53 intervals of the system, by an extension of the ordinary notation for the seven notes of the octave C, D, E, ... In fact the intervals C to D, D to E, F to G, &c. consist of a five-fifth and a seven-fifth semitone, which together make nine intervals in the system of 53; while E to F and B to *c* are each a five-fifth semitone or four intervals, and of course $5\times 9+2\times 4=53$. Also any note is sharpened by raising it a five-fifth semitone, and flattened by depressing it a seven-fifth semitone. If now we denote the successive notes in the system of 53 by the numbers 1, 2, 3, ... 53, 54, ... and call C, 4, then C♯ or D♭ is 8, D is 13, ... A♯ or B♭ is 48, B is 53, *c* is 57, &c. Thus we have twelve notes corresponding exactly to the seven white and five black keys of an octave on the piano, except that the intervals from C to C♯ and from C♯ to D are in the ratio of 4 to 5 instead of being equal. The notation for the other notes is now easily stated. A mark of elvation (/) or a mark of depression (\) put before a letter signifies a note an interval higher or a note an interval lower than that denominated by the letter; two marks signify a note higher or lower by two such intervals; and so on. The whole of the fifty-three notes of the octave can now be indicated; *e. g.* nos. 3, 4, 5 are \C, C, /C. Nos. 7, 8, 9 are \C♯, C♯, /C♯, and so on. Under certain circumstances the same note could be indicated by either of two notations; *e. g* No. 7 could be indicated by //C or \C♯, indifferently. It is to be observed that all these notes can be easily written on the musical staff.

These notes all admit of being played on a harmonium furnished with a key-board (called a generalized key-board) resembling that of a piano, but in which each key of the piano is replaced by seven keys one above another—an octave of the whole key-board consisting of seven tiers of keys, 84 in all. In the arrangement of the keys, every note determined by an exact fifth is placed a quarter of an inch further back and a twelfth of an inch higher that that which precedes it in the series of fifths—*e. g.* G is set a quarter of an inch further back and a twelfth of an inch higher than C. "The most important practical point about the key-board arises from its symmetry—that is to say, from the fact that every key is surrounded by the same definite arrangement of keys, and that a pair of keys in a given relative position corresponds always to the same interval. From this it follows that any passage, chord, or combination of any kind has exactly the same form under the fingers in whatever key it is played" (p. 20).

This statement, it will be observed, is an answer to what we may call Dr. Stainer's challenge. We may just add that any system

* In fact $5(7x-4y)+7(-5x+3y)=y$; the above statement is therefore true whether the fifths be exact or approximate.

of dividing the octave which can have its notes arranged in a continuous series of equal fifths, and which returns to the same pitch after a certain number of fifths, is called a regular cyclical system; and it is of the rth order, positive or negative according as twelve of its approximate fifths exceed or fall short of seven octaves by r units of the system. Thus the system of 53 is merely a particular case of a regular cyclical system; and it is of the first order positive, because $12\times31-7\times53=1$.

In addition to the discussion of the positive systems, the mean-tone or old unequal temperament is described, and some interesting historical notices concerning it are given, in Chapters V. and VI., as well as suggestions for adapting the generalized key-board (with a smaller number of keys) to it. "The result of the writer's practical experience is, distinctly, that there are many passages in ordinary music which cannot be adapted with good effect to positive systems —and that the rich and sweet masses of tone which characterize these systems, with the delicate shades of intonation which they have at command, offer to the composer a material hitherto unworked. The character of music adapted for these systems is that of simple harmony and slow movement: it is a waste of resource to attempt rapid music; for the excellence of the harmonies cannot be heard. The mean-tone system is more suitable for such purposes" (p. 73).

We cannot say that the arrangement of the book is satisfactory; a reader would probably be disappointed who goes to it hoping to find an elementary discussion of musical intervals, such as a learner would make out without excessive trouble, and such as the title-page appears to promise. To mention a single point; we cannot help thinking that it would have been much better if the author had assumed explicitly that his readers were able to use a common table of logarithms of numbers, instead of setting them to reduce a certain formula to numbers—a process which is in fact that of calculating the logarithms for themselves. We do not see that the least advantage is gained by not employing "the labours of those who constructed the tables of common logarithms" (p. 88). However, it is not fair to press this point, as the author himself allows that "the arrangement [*i. e.* of his book] is unsatisfactory from a scientific point of view" (p. vii); but we must be allowed to add that it seems to us unsatisfactory also from the point of view of elementary exposition.

LIII. *Proceedings of Learned Societies.*

ROYAL SOCIETY.

[Continued from p. 310.]

April 12, 1877.—Dr. J. Dalton Hooker, C.B., President, in the Chair.

THE following paper was read:—

"On certain Molecular Changes which occur in Iron and Steel during the separate acts of Heating and Cooling." By Professor Norris, M.D., Queen's College, Birmingham.

In the course of certain researches in Physiological Physics, in which the author of this paper has been for some time past engaged,

it became necessary, with a view to learn how far it bore upon the subject in hand, to inquire into the nature of a peculiar fact which was observed by his friend Mr. Gore, and published in the Proceedings of the Royal Society, January 28th, 1869, under the title of "A Momentary Molecular Change in Iron Wire." In this communication it was shown that if a strained iron wire were heated to redness by a voltaic current or other means, on being allowed to cool, the contraction of cooling was at a certain point, and for a limited period, arrested by an action of elongation.

"With wires of iron 0·65 millim. thick (No. 23) and 21·5 centims. long, strained to the extent of ten ounces or more, and heated to full redness, the phenomenon was clearly developed. For example, the needle of the instrument went with regularity to 18·5 of index-plate; the current was then stopped; the needle instantly retreated to 17·75, then as quickly advanced to 19·75, and then went slowly and regularly back, but not to zero. After shutting off the source of heat, the wire contracted 0·75 millim., and then expanded 2 millims., so that it returned 1·25 millim. beyond the original point of heating, and then resumed its course towards zero, which it failed to reach The length of the kick, plus the amount of stretch, occasioned during the occurrence by the strain, was therefore 2 millims. If the temperature of the wire were not sufficiently high, or the strain upon the wire not enough, the needle went directly back without exhibiting the momentary forward movement. The temperature and strain required to be sufficient to actually stretch the wire somewhat at the higher temperature. A higher temperature with a less degree of strain, or a greater degree of strain with a somewhat lower temperature, did not develop the phenomenon. The wire was found to be permanently elongated on cooling."

Mr. Gore further observes:—"The molecular change evidently includes a diminution of cohesion at a particular temperature during the process of cooling; and it is interesting to notice that at the same temperature during the heating-process no such loss of cohesion (nor any increase of cohesion) takes place; a certain temperature and strain are therefore not alone sufficient to produce it; the condition of cooling must also be included. The phenomena which occur during cooling are not the exact converse of those which take place during heating."

The subject was subsequently taken up by Professor Barrett, of Dublin, who, in a paper to the 'Philosophical Magazine' in 1873 (vol. xlvi. p. 472), showed, by the use of the mirror, that during the heating of the wire a converse action to that which takes place during cooling occurs. He says:—"During the heating of the wire a slight and momentary retrogression of the beam was noticed at the temperature corresponding to the powerful jerk that occurred on cooling.

"The temperature at which the momentary jerk occurs seems to be lower in thick wires than in thin ones. The momentary *retraction*, as closely as can be judged, takes place at the same temperature at which the *elongation* takes place on cooling. Releasing the tension of the spring, the forward motion on cooling is, as

might be expected, much lessened, whilst the jerk back is scarcely affected. Increasing the tension of the spring, the forward jerk is correspondingly increased, and the backward jerk diminishes and can be made to disappear. Without the spring, an iron wire can be seen by the naked eye to undergo a momentary contraction during heating, and a momentary and more palpable elongation during cooling.

"All kinds of iron do not exhibit this behaviour; and some show it in a more or less marked degree. I have not been able to detect any change in certain specimens of good soft iron wire; but in hard iron wire, and notably in steel wire, it is very apparent.

"The wire, moreover, requires to be raised to a very high temperature before the jerk is seen on cooling. I have not observed the momentary elongation on cooling when the wire has only been heated to a point just beyond that at which it would otherwise occur.

"During the cooling of the wire it was found that just as it reached a very dull red heat, a sudden accession of temperature occurred, so that it glowed once more with a bright red heat. It was found that the reheating of the wire occurred simultaneously with the momentary elongation."

In studying these phenomena it seemed, in the first place, desirable to construct apparatus of much greater delicacy and heating-power than that used by either of the previous observers, so that, if possible, the shortening during heating could be shown with the same facility as the elongation during cooling. This has been achieved by means of the instrument a sketch of which is given with the Charts. The main idea has been to construct an apparatus which would exhibit the phenomena readily without the use of mirrors or batteries, and that would admit of experiments being performed either with or *without strain*. This latter has been accomplished by placing the wire vertically, so as to get rid of all drooping when heated. With apparatus thus constructed, we found no difficulty in displaying the phenomena in the most perfect manner, the heating-kick not unfrequently being three or four centimetres in length, and the cooling-kick sometimes as much as 13 centimetres.

It is necessary to state *in limine* that *strain* plays no part in the production of the phenomena of the kicks or jerks. Its only effect is to cause a very small influence in the cooling (which might have been overlooked with certain kinds of apparatus) to be observed. It is obvious that when a wire has a tendency to expand, the presence of weight or tension, by assisting to overcome the inertia of the apparatus, would favour the exhibition of the act; but it is equally clear that it would operate in an opposite manner when the tendency was to contract, as in the heating; and therefore, although it would favour the cooling, it would be prejudicial to the heating-kick.

Strain, therefore, being *unessential* to the phenomenon, and, by the introduction of false quantities, prejudicial to the quantitative comparison of the several effects, it has been carefully avoided in these experiments, sufficient weight alone being used to keep the thread tense upon the pulley, and never in any case to elongate the par-

ticular wire under use, even when maintained for some time at its highest temperature.

It is desirable that these facts should be borne in mind; for no sooner do we enter upon this research with more delicate and reliable apparatus, than we find that the kicks are but a small part of the phenomena we are called upon to observe and explain. We ascertain at the very outset that iron and steel wire presents itself to our examination under very different conditions, which demand a rigid analysis. Thus, apart from its inherent quality, it may come to us for experiment:—

(*a*) In its usual commercial state.

(*b*) After having been subjected to various degrees of annealing.

(*c*) In various degrees of induced hardness.

It is proposed to consider, in the first place, the phenomena presented by the ordinary steel wire of commerce, when *first* subjected to the influence of heat. During the heating of such wires, we notice that a first kick occurs at a point varying on the scale from 29° to 33°, and that the wire subsequently proceeds to a high expansion, which may be represented on the scale by the figures 66°, 52½°, 55°, 50½°, and so forth, according to the quality and state of the wire. In the act of cooling a kick commences at points varying from 31½° to 22°, and terminates at points varying from 33° to 28°, when the finger proceeds on towards zero, but *invariably falls short of reaching it by amounts varying from* ½° *to* 5½° (*centimetres*). [*Vide* fig. 1, p. 394.]

In the next experiment with these wires a much altered state of things is found to obtain. Thus the first kick is lowered a little in position, increased in range; the expansion of the wire is materially diminished, being now represented by such figures as 58½°, 43½°, 45½°, 50¾°, &c. respectively. In the cooling the second kick is separated more from the first, being put back in the direction of zero. It will also be seen that in cooling the finger passes *beyond zero*, indicating now that the wire is *permanently shortened*, whereas in the primary heating it was *permanently elongated*.

A comparison of these two series of experiments will show us that, during the heating of these wires, there is going on at the same time a whole series of phenomena, some of which, although different in nature, are alike as to result, while others are different both as to nature and result. We have, in the first place, the ordinary expansion, which we will designate the "dynamical expansion." In the primary heating an amount of expansion will be seen to occur which has no equivalent in the dynamical contraction of cooling. The secondary heatings reveal to us the existence of a contraction, which is also excited *during the heating*, and the action of which is to limit the dynamical expansion previously referred to. That it *masks* a portion of the dynamical expansion is rendered obvious by the fact that, in cooling, the finger moves *beyond* zero, showing that the wire has contracted more in cooling than it expanded in heating.

In addition to this, we have also the phenomena of the kicks themselves; and these may be described as consisting of a *temporary* contraction and expansion.

During the heating of a wire, when in its commercial state, there are one expansive and two contractive tendencies exerting their powers at one and the same time; and conversely, in the *act of cooling*, there are one contractive and two expansive influences at work, viz.:—ordinary cooling contraction; an expansion which is the opposite of the temporary contraction of heating—*the cooling-kick*; and an expansion which is the opposite in nature, but not necessarily in amount, of the contraction of heating—*crystalline expansion*. In every case the interpretation of the general result depends upon the accurate estimate of the extent to which these interacting forces have modified each other's effects. Thus during the heating we have a temporary and a permanent contraction, assisting each other to oppose the dynamical expansion. In cooling, on the other hand, we have two expansions, one of which is temporary and the other permanent, opposing the dynamical contraction of cooling.

It will be desirable to carefully define the nature of these respective influences, and the terms which will be used to distinguish them in this research.

I. *Dynamical Expansion*.—This term will be used to distinguish the ordinary dilatation produced in bodies generally, by raising them from a given temperature to a higher one, and which is exactly counterbalanced by contraction when the original temperature is regained. It is proposed to call this kind of contraction "the dynamical contraction."

II. *Contraction of Heating*.—In the diagrams representing second heatings [*vide* fig. 2] we get the first inkling of the existence of a contractive or shortening influence excited by heat simultaneously with the expansion. In the diagrams of annealed and hardened wire [*vide* figs. 3, 4, 5] this influence becomes more obvious still. In these cases it is seen to greatly *mask* the dynamical expansion. This kind of contraction may be also displayed by protracted heating of the wire, when it exhibits itself at the end of the expansion as a slow, continuous contraction of considerable extent [*vide* fig. 5].

III. *Temporary Contraction*.—This term is applied to the cooling influence which is excited in the wire during heating, and which, at a certain point, balances the expansion; for heat being rendered latent at the same rate as it is being absorbed, produces a stop (which indicates that the expansion is arrested and balanced) or a kick (which implies an absolute cooling of the wire from excess of latency). The diminution of the rate of expansion, or the actual shortening produced by this kind of contraction, is of a temporary character, and must not be confounded with the heat-contraction which it accompanies.

These, then, are the phenomena of heating:—

(1) Dynamical expansion;
(2) Permanent or heat contraction;
(3) Temporary contraction (heating-kicks);
(4) Stretching; and
(5) The influence of oxide.

We have now to consider what influences are present during the cooling:—

I. *Dynamical Contraction.*—The opposite of dynamical expansion.

II. *Permanent Expansion* of cooling.—(Crystalline expansion.)

III. *Temporary Expansion.*—The *thermal* expansion due to the reglowing of the wire during cooling. This is the proximate cause of the stops and kicks which occur in cooling. It is evanescent as an opposing force, and must not be confounded with the permanent or crystalline expansion of cooling, of which it is simply the effect.

We have, then, in cooling:—

(1) Dynamical contraction;
(2) Permanent expansion of cooling;
(3) Temporary expansion (cooling-kicks); and to these may be added
(4) Influence of oxide.

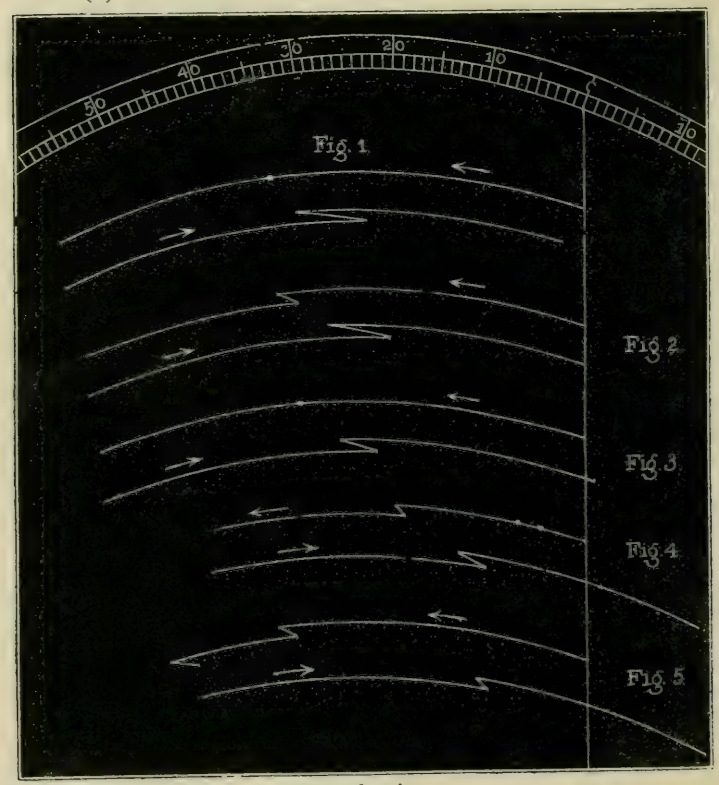


Fig. 1. Commercial steel wire. First heating.
Fig. 2. Do. do. Second heating.
Fig. 3. Air-hardened wire.
Fig. 4. Water-hardened wire.
Fig. 5. Annealed steel wire. High-temperature contraction. Contraction returns.

N.B.—In each figure the upper curve refers to the heating, the lower to the cooling effect.

An extended study of these various conditions has led to the elucidation of the nature of hardening, softening, tempering, annealing, &c. of iron and steel, and has further shown that numerical values may be assigned to these states.

In brief, the research establishes:—

1. The existence in steel, and in iron containing *free* carbon, of a contraction or shortening which is excited by heat, and which proceeds simultaneously with the dynamical expansion and masks its true amount. This is divisible into *high* and *low* temperature contraction. [Compare figs. 4 & 5.]

2. The presence of a cooling expansion or crystallization, which comes in during the dynamical contraction and masks its true amount.

3. These effects, due to crystallization and decrystallization, are the causes of the so-called kicks, or temporary contractions and expansions, which occur during the heating and cooling of the steel.

4. That the low-temperature contraction and cooling expansion are due to decrystallization and crystallization which occur during the acts of heating and cooling, while the kicks themselves are simply the thermal effects associated with these changes, and are proportionate to their extent.

5. That protracted annealing (that is, *extremely slow cooling*) brings about molecular separation of the carbon and iron; and steel in such a state contracts greatly when high temperatures are reached, producing the *contraction returns* seen at the end of the heating, and which are due to the condensation produced by the recombination of the carbon and iron. Steels in this state are less susceptible to cooling-expansion (crystallization), and therefore to low-temperature contraction on subsequent heating. [*Vide* fig. 5.]

LIV. *Intelligence and Miscellaneous Articles.*

FRESH RESEARCHES ON THE METAL DAVYUM. BY M. SERGE KERN.

AS I intimated in my first Note addressed to the Academy, my ingot of davyum weighed 0·27 grm. The metal was dissolved in aqua regia in order to examine the action of different reagents upon the solution.

Potass gives a bright yellow precipitate of hydrate of davyum, which is readily attacked by acids, even by acetic acid. The hydrate dissolved in nitric acid gives a brownish mass of nitrate of davyum; on calcining this salt, a black product is obtained, which is probably the monoxide.

The chloride, dissolved in a solution of potassic cyanide, gives, when the solution is slowly evaporated, beautiful crystals of a double cyanide of davyum and potassium. The potassium in this salt can be replaced by several metallic elements. Cyanodavic acid is very unstable; it is isolated by passing a current of sulphuretted hydrogen through a solution of a double cyanide of lead and davyum.

In acid solutions of davyum sulphuretted hydrogen produces a precipitate of sulphuret of davyum, which is readily attacked by the alkaline sulphurets, probably giving a series of sulpho-salts.

A concentrated solution of davyum chloride gives, with potassic sulphocyanide, a red precipitate which, slowly cooled, produces large red crystals. If the same precipitate is calcined, the davyum sulphocyanide takes the form of a black powder. These reactions show that this salt is allotropic.

The chloride is very soluble in water, alcohol, and ether; but the crystals of this salt are not deliquescent. Calcined, the salt gives as residue the monoxide. The chloride of davyum forms double salts with the chlorides of potassium and ammonium; they are insoluble in water, and highly soluble in absolute alcohol. The double salt of sodium and davyum is almost insoluble in water and in alcohol; this reaction is characteristic, because several sodic salts of the platinum group are highly soluble in water.

This chloride of davyum is the only one that exists, as the second product, containing more chlorine, decomposes during the evaporation of the solution, liberating chlorine.

I have made some new researches upon the density of cast davyum; three experiments gave the following numbers—9·388, 9·387, 9·392 at 24° C.

These results agree very closely with those of my first trials: the density given in my first Note was 9·385 at 25°.

M. Alexejeff, engineer, has undertaken the determination of the equivalent of davyum; but as the quantity of the metal which I possess is very trifling, accurate results are very difficult to obtain. Some preliminary experiments have shown that the equivalent is above 100, and probably not far from 150–154.

An additional quantity of platiniferous sand which will be placed at our disposal will give a sufficient supply of the new metal for fresh experiments; we expect to have, in a little time, about 1·2 gramme of davyum.—*Comptes Rendus de l'Académie des Sciences*, October 1, 1877, tome lxxxv. pp. 623, 624.

THE GAMUT OF LIGHT. BY PLINY EARLE CHASE.

In accordance with a suggestion of Dr. Henry Draper, that I should test some of my views by the spectral lines, I have undertaken a preliminary investigation, with the following result.

In the harmonic progression, $\frac{c}{n}$, $\frac{c}{n+a}$, $\frac{c}{n+2a}$, &c., let c = wave-length of Fraunhofer line A, =761·20 millionths of a millimetre; n=1·015, a=·0918, and we find the following accordances:—

Numerator.	Denominators.	Quotients.	Observed.	Kirchhoff.
761·20	$n+a$	687·75	687·49 B	592·7
	$n+2a$	635·07	634·05	783·8
	$n+3a$	589·89	589·74 D_γ	1005·1
	$n+4a$	550·72	550·70	1306·6
	$n+5a$	516·42	517·15	1655·6
	$n+6a$	486·14	486·52 F	2080·0
	$n+7a$	459·22	458·66	2436·5
	$n+8a$	435·12	435·67	2775·7
	$n+9a$	413·43	?	?
	$n+10a$	393·79	393·59 H′	H′

The "observed" values are the wave-lengths, as determined by Dr. Wolcott Gibbs (Amer. Jour. Sci. [2] xliii. p. 4), of the corresponding lines on Kirchhoff's scale. It seems likely that $\frac{c}{n}$ may be a *bright* line, and thus belong to the new field of investigation which Dr. Draper has opened by his paper on the discovery of oxygen in the sun. The doubtful line (?) is midway between Kirchhoff's line $2869{\cdot}7=430{\cdot}37$, and $H=397{\cdot}16$.

As alternate planets in the solar system, so alternate Fraunhofer lines appear to obey the simplest law, intermediate values being governed by laws of mutual equilibrium. The figurate symmetry of the denominators for those alternate lines ($n+a$, $n+3a$, $n+6a$, $n+10a$) is specially noticeable, and suggestive of my equation between the principal planetary masses:—

$$(\text{Neptune})^{1}\times(\text{Uranus})^{3}\times(\text{Jupiter})^{6}\times(\text{Saturn})^{-10}=1.$$

Haverford College,
August 23, 1877.

ON THE FLUORESCENCE OF THE LIVING RETINA.

BY M. VON BEZOLD AND DR. G. ENGELHARDT.

Studies on the laws of colour-mixture, some years since, suggested to one of us the question whether the fluorescence observed by Helmholtz*, and afterwards by Setschenow †, in the dead retina could not also be demonstrated in the living structure. Experiments made at that time, however, gave no result, but rather led to the conviction that the solution of this problem would be possible only in conjunction with an ophthalmologist.

Interest in this subject was awakened afresh by the path-opening discoveries of Boll and Kühne, since through them all inferences from the dead to the living retina must appear in the highest degree doubtful. This induced us to attack the investigation jointly, the results of which are communicated in the following.

Before all things it seemed requisite to observe ophthalmoscopically the retinal picture of a spectrum, and then to try if it could be displaced so far behind the pupillar margin that at last we should have before us the retina in ultra-violet illumination only. To this end the fan of coloured rays issuing from the prism was received by the speculum so near that the whole of it fell upon the latter. Then, by a suitable choice of distances and of the lenses employed (the observations were always made on the inverted magnified picture), it was possible to produce on the retina so small a picture of the spectrum that the whole of it, or at least the greatest part, could be viewed simultaneously.

The result was a very surprising one, and, although at the commencement neither sun-light nor quartz prisms were employed, already contained in itself the wished-for issue, which, it is true, had then to be rendered perfectly capable of demonstration by varying and perfecting the experiments.

The retinal picture of a spectrum shows, namely, peculiarities

* Poggendorff's *Annalen*, vol. xciv. p. 205.
† *Arch. f. Ophth.* vol. v. p. 205.

which are conditioned partly by the absorption-phenomena of the blood, and in part by fluorescence. The aspect of this picture is extremely beautiful. While the retinal background shows the picture of the spectrum in the usual manner, the vessels stand out in very various colouring: shown upon the red background only by a somewhat intenser tint, in the orange almost absolutely unrecognizable, they appear in the green deep black in wonderfully sharp outline, but in the blue in a dark brown-yellow tint, which becomes in the violet a dark red-brown. In the orange they are so feebly prominent that one might think they were filled with water, while, on the contrary, at the commencement of the green they become suddenly as black as if they contained ink; and this leap from the one into the other tint takes place in such a striking manner that they appear almost as if cut off. As is well known, in feebly luminous spectra pure yellow is not perceptible; we know, however, from experiments on the absorption of blood that it commences in the region of Fraunhofer's line D, and, indeed, a little preceding it, as follows from the fact that the vessels when illuminated with the light of sodium are likewise seen black.

Accordingly, as far as into the green the phenomenon described corresponds closely to what might have been expected from the absorption-spectrum of blood.

In the blue, however, in the region of the line F, things are changed. If we had here to do with absorption-phenomena only, the vessels would of necessity be marked similarly as in the red—that is, merely by a difference of brightness—although somewhat more sharply; we might then expect merely darker blue vessels upon a moderately bright ground. Instead of this, they appear in a yellowish brown tone, reminding one of very dark ochre, while in the violet they show a decided tendency to red, somewhat like rusty iron.

This phenomenon can only be explained by fluorescence of the underlying retina; and thus the vessels of the retina furnish the finest test of the presence of fluorescence.

At the first instant, one might indeed think that the phenomenon was one of contrast; but a somewhat closer consideration teaches us that this supposition is here inadmissible. For, in the first place, one could not perceive why the phenomenon should be absent from the green, which yet we know to be specially apt to call forth contrast-phenomena; and then the colour of the vessels would necessarily approach yellow-green from the blue to the violet, while, on the contrary, the dark brown of the vessels passes over into red-brown in this region of the spectrum.

Moreover fluorescence of the blood itself cannot be the cause, since we at least have not succeeded in discovering in blood a trace of fluorescence; besides, it would be extremely improbable that, in transmitted light, red blood should show red fluorescence.

Just as little can the cause be sought in diffused light that in some way has penetrated into the eye, or, in any case, find its origin in the fluorescence of the cornea or the lens; for such light must show its action equally in the green portion of the spectrum—nay, there in increased measure, since the contrast must sharpen the

impression*. Moreover fluorescence-light issuing from parts of the eye situated *in front of* the vessels of the retina could not but make itself perceptible, even in viewing Purkinje's figure in monochromatic illumination—which, according to our observations, is not the case.

The peculiar brown and red-brown colouring of the retina-vessels in the blue and violet parts of the spectrum, can consequently be explained only by fluorescence of the retina situated behind them; indeed the commencement of it must be sought in the same place in which it was found by Helmholtz in the dead retina.

Although, according to what has just been said, the fluorescence of the living retina has already been proved by this one experiment, yet we were not willing to rest satisfied with this, but to pursue the matter still further in different directions, in order thus to procure further material of proof. In the first place we endeavoured to imitate the phenomena seen upon the retina; for we brought a capillary tube filled with blood-solution before a spectrum projected upon a surface. Here also exactly the same phenomena were seen in the red, orange, yellow, and green, in the blue and violet likewise when the screen fluoresced in these colours. It is true that here the slightest trace of fluorescence is perceived, so that even white paper permits it to be distinctly recognized; and the colour of the tube before such a screen reminded one, in all parts, of the blood-vessels on the retina; that here, however, we had in fact to deal with the light of fluorescence which issued from the screen was strikingly shown by this—that the brown and reddish colouring of the capillary tube totally vanished when the screen was removed so that the black space of the dark room served as background, and that it came up much more decidedly when for the white paper screen one coated with platinicyanide of barium or other fluorescent substances was substituted. These experiments convinced us that, in a transparent coloured substance held before another body serving as projection-surface for a spectrum, we possess an extremely sensitive means for the recognition of traces of fluorescence. Whenever this test substance, in a part of the spectrum in which it when alone does not permit its natural colour to be recognized, shows it if there is a body behind it, this must be the result of fluorescence-light emitted from the latter body.

Shadow-streaks were also called forth in a projected spectrum, in order to distinguish with complete certainty the influence which contrast-phenomena might possibly in any case exert upon the observation. The conclusion was, that the colour of the retina-vessels observed in the blue and the violet is in no case the consequence of phenomena of contrast.

After settling this more physical side of the matter, the question now was, to further extend the ophthalmoscopic investigations and vary them in divers ways; for the method above-mentioned, in which the entire fan of coloured rays is taken up by the speculum and a minute spectrum is thrown upon the retina, is not free from

* With very intense illumination this kind of light actually does appear to assert its influence; and on this account moderate illumination of the retina is to be preferred.

the objection that in this way a perfectly pure spectrum is with difficulty obtained. It almost needs a lucky accident for the position of the lenses and the accommodation of the eyes to cooperate so favourably that the eye observed sees distinctly the Fraunhofer's lines at the same instant in which the observer has the background of the eye sharply before him. Now, although a slight deviation from perfect purity cannot do much harm when the blood-vessels are made use of as a criterion of fluorescence, and consequently the mere superficial judgment of the observer is enough for the attainment of sufficient purity, yet it was still desirable to entirely obviate the objection mentioned. This was done in the following manner :—

By means of a large, powerfully dispersing, direct-vision prism, a spectrum was projected of 40–50 centims. length. The observer now repaired to the region of the image-plane, and caught with the speculum now this, now that sort of rays, so that the observed eye was successively illuminated with nearly monochromatic light of various degrees of refrangibility.

The colour of the vessels appeared every time exactly as it did with the method above described—and, indeed, not only with the brown rabbit usually made use of for the experiments, but also with man.

This mode of investigating is much more convenient than the above-described ; but it involves the impossibility of seeing all the phenomena at one view.

At first all the experiments were made with lenses and prisms of glass, and partly, indeed, using only a skioptikon as the source of light. It now appeared desirable to repeat them with quartz lenses and prisms, when, of course, sunlight was employed ; but herein it was not possible to use the second mode of observation, since the spectrum could not be rendered sufficiently large. On this account we were compelled always to project a somewhat larger portion of the spectrum upon the retina.

The results were in general the same as those above described ; only the brown-red colouring of the blood-vessels came out more vividly than when glass apparatus was employed (the speculum, however, and the lenses belonging to it were still of glass) ; and, finally, it was in this case possible to trace the phenomenon as far as into the ultra-violet. *After the entire visible spectrum was intercepted, being gradually brought to vanishing behind the pupillary margin, so that only ultra-violet rays fell upon the retina, the vessels of the retina appeared in a decidedly reddish tone upon a dirty grey-brown ground.*

To sum up, by these observations it appears to us demonstrated *that the living retina also does actually fluoresce, and under the influence of the same rays which Helmholtz had already recognized as exciting fluorescence in the dead retina.*

As a mark of fluorescence the colour of the retina-vessels served, which in blue, violet, and ultra-violet light approached more and more to the natural colour of the blood—a fact only to be accounted for by fluorescence of the layers situated behind them.—*Berichte d. baier. Akad., math.-phys. Classe,* July 7, 1877.

THE

LONDON, EDINBURGH, AND DUBLIN

PHILOSOPHICAL MAGAZINE

AND

JOURNAL OF SCIENCE.

[FIFTH SERIES.]

DECEMBER 1877.

LV. *On the Thermal Conductivity and Diathermancy of Air and Hydrogen.* By Dr. Henry Buff, *Professor of Physics in the University of Giessen**.

MORE than fourteen years ago Magnus published experimental researches†, the results of which led him to conclude that hydrogen possesses a thermal conductivity resembling that of the metals. This conclusion, though not entirely unobjected to, has since passed into most physical textbooks.

Doubts as to the correctness of this assumption have of course no reference to the capacity possessed by hydrogen, as well as other gases, of conducting heat in a small degree independent of accompanying currents. These doubts also are not removed by the observations of Kundt and Warburg‡, which prove the thermal conductivity of hydrogen to be, indeed, considerably greater than that of other gases ; for this is quite possible without assuming that the conducting-power of hydrogen approximates as nearly to that of the metals as Magnus thought necessary to assume, in order to explain such phenomena as the incandescence of platinum wire, first observed by Grove. True, Magnus did not think himself justified in supposing that in this experiment a greater decrease of the temperature of the platinum wire in the hydrogen was caused by a more rapid current of the gas. "It is not evident," he said, "why currents, produced by differences of temperature, should

* Communicated by the Author.

† Pogg. *Ann.* Bd. cxii. S. 497. [Phil. Mag. July 1861, p. 1.]

‡ Ibid. Bd. clv. S. 337. [Phil. Mag. July 1875, p. 53.]

be stronger in hydrogen than in other gases." Such difference in the behaviour of air and hydrogen, apart from the greater mobility of the latter, could not possibly exist, if the two gases (equal volumes of which, at the same pressure, have the same specific heat) possessed also equal thermal conductivity and equal diathermancy.

Designating the weight of v cub. centims. of a gas as usual by

$$p = \frac{273 \,.\, vbd}{1000 \,.\, 760(273+t)},$$

where d is the weight of 1000 cub. centims. at 0° and 760 millims. pressure, b the tension, and t the temperature, then the difference of weight, or the upward pressure of v cub. centims. of this gas, which in the cooler medium at t has risen to the higher temperature t', will be

$$\frac{273vbd}{1000 \,.\, 760}\left(\frac{1}{273+t}-\frac{1}{273+t'}\right)=\frac{273vbd}{1000 \,.\, 760}\cdot\frac{t'-t}{(273+t)(273+t')}$$

This gives the quotient of the upward pressure through the mass, and consequently the acceleration

$$C=\frac{g(t'-t)}{273+t}.$$

If, therefore, different gases obtain equal accelerations for the same difference of temperature $t'-t$, this ceases to be the case as soon as a change in the difference of temperature takes place. But this latter must always happen if the specific heats of any two gases, and more especially their capacities of absorbing or losing heat in contact with solid bodies, are not the same. So far, then, there is no need of assuming a metal-like conductivity of hydrogen, in order to explain the more rapid abstraction of heat by this gas. It is sufficient to know that, though a bad conductor, its conducting-power is superior to that of other gases.

Magnus's own experimental results appear to us much more favourable for his hypothesis. The apparatus he employed was essentially as follows*:—Onto a cylindrical vertically placed vessel of thin glass 56 millims. in diameter and 160 millims. in height, there was fused another, open glass cylinder of equal diameter, but of only 100 millims. height, in such a manner as to separate both vessels by only a thin glass plate. Through the cork which closes the lower opening of the cylindrical vessel pass two glass tubes provided with stopcocks, by means of which the vessel may be filled with air or any other gas at any desired pressure. About 50 millims. below the separating plate is a tubulature for the insertion of a ther-

* Phil. Mag. [IV.] vol. xxii. p. 5, pl. i.

mometer fixed in a horizontal position. The upper vessel is filled with boiling water, which, during the experiment, is kept in ebullition by the introduction of steam. To keep the surrounding medium at as constant a temperature as possible, the apparatus is placed in a beaker, and this again in a second beaker filled with water of a constant temperature to the height of the boiling water in the inner vessel.

In order to diminish radiation as far as possible, a cork disk, or a thin silvered copper plate, was placed as a screen above the bulb of the thermometer. But the desired object was very imperfectly attained in this way; for the thermometer stood 8 degrees higher than that indicating the temperature of the water in the outer beaker, even when the air was almost entirely exhausted. On allowing air to enter, this rise of temperature diminished more and more with the increase of pressure, thus proving that, as in solid and liquid bodies, the heat-rays are partially absorbed by their passage through air. Conductive motion, if such existed, was masked by the stronger effect of radiation.

Similar results were obtained by Magnus with a great number of other gases investigated by him. With hydrogen, on the contrary, he found that the temperature increases with the increase of density; and even at ordinary atmospheric pressure it has a greater diathermancy than a vacuum.

It was more especially on account of this behaviour that Magnus inferred the similarity of hydrogen to the metals as regards the conducting-power.

A more minute and careful investigation of the above method led me, however, to a different conclusion, and eventually to a renewed experimental investigation.

My apparatus is similar to that used by Magnus, with such alterations as seemed to me appropriate. My object being to study the conductive power of gases, other influences being excluded (such as the effect of radiating heat &c.), a brass cylinder, instead of that of glass in Magnus's apparatus, was cemented air-tight upon the glass vessel. The bottom of the cylinder facing the thermometer is a polished clean metallic surface; a double wall surrounds it, the space between being filled with cotton-wool to prevent too rapid cooling. The glass cylinder is 20 centims. high and 7·5 centims. in diameter; its lower edge is ground so as to fit air-tight onto the plate of an air-pump. Through the plate (of the air-pump) pass two wires, one of iron and the other of German silver, and extend vertically almost to the bottom of the brass cylinder, where they are soldered together. At the junction both wires are flattened to 12·5 millims. width, and thus form a flat arc whose centre was, in the first experiments, only 23 mil-

lims. below the metal plate. The two exterior ends of the wires, near each other but well insulated, are connected by means of copper wires with an astatic galvanometer. Both are surrounded by a thick covering of cotton-wool to protect them against sudden alterations of temperature.

The substitution of a thermoelectric pile for the mercurial thermometer has in the first place, like the metal plates of the brass cylinder, the object of diminishing the influence of radiation ; but, besides that, it is more sensitive to thermal influences than the latter, on account of the adjustment of the soldered junction.

In the first experiments a strip of silver was placed above the soldered junction as a screen to protect it from radiation ; but in later experiments, on finding this precaution superfluous, it was removed. Magnus had found that the advantage he had expected to derive from the use of the screen was more than counterbalanced by the screen itself becoming warm and communicating heat to the sides of the vessel. This I found to be the case in my experiments also.

The whole apparatus is surrounded by a wider glass cylinder, the ground edge of which fits onto the plate of the air-pump. The space between this outer cylinder and the apparatus can therefore be filled with cold water. I, however, like Magnus, did not at first use the cooling arrangement.

The very first experiments disclosed a source of error, which had to be eliminated. The hot water in the brass cylinder not only heated the junction of the thermoelectric pile and the air surrounding it, but also, very probably to a higher degree, the sides of the glass cylinder, both by conduction and radiation. The increase in temperature was perceptible even to the touch, and extended to below the level of the soldered junction.

It is thus evident that a current of gas ascends along the sides of the glass, and hence the experiments were useless, as far as the question of the conductivity of the gases is concerned.

Magnus had certainly noticed this influence of the heated sides of the glass cylinder ; but he probably failed to appreciate its importance, inasmuch as by his method of observation the sides of the cylinder were not accessible*.

I had hoped to eliminate this error by abbreviating the duration of the experiment. Magnus maintained during the whole experiment the temperature of the heating-vessel at the boiling-point by the introduction of steam. As the mercury thermometer required from 20 to 40 minutes to reach its maximum, it is evident that the heat had ample time to extend through the whole apparatus.

* Compare the drawing of his apparatus in Phil. Mag. vol. xxii. pl. i.

I had observed that, if the hot liquid in the brass vessel was allowed to cool freely, the astatic needle nevertheless after some time assumed a maximum deflection, indicating a state of equilibrium between the influx and loss of heat. It is known that tolerably strong deflections of the needle of a highly sensitive galvanometer correspond to but slight alterations of temperature at the soldered junction. If, therefore, we know the temperature of the brass vessel (or rather that of its bottom) at the commencement of the experiment, and the temperature of its fluid contents for which the deflection of the needle is greatest, then the thermal equilibrium, upon which the highest temperature at the soldered junction depends, must be very nearly proportional to the difference of those two temperatures of the brass vessel, at least so long as the thermal differences are small.

Accordingly the brass vessel, at the commencement of the experiment, was filled with water at such temperature that the needle pointed to 0° and remained stationary. This having been effected, part of the cold water was taken out and replaced by hot water; the temperature of the mixture was observed, and simultaneously the time of pouring in was noted. The temperatures were taken by a thermometer whose bulb was in contact with the bottom of the brass vessel.

The following Table gives the chief results of some of the experiments carried out in this manner. The figures in the column marked T record for each of the stated gases the temperatures of the water :—first, at the commencement of the experiment; secondly, after mixing the hot and the cold water; and, thirdly, at the moment when the deflection of the needle was at its maximum. The differences between the first and third figures are given under t; whilst τ shows the greatest corresponding deflections, whose real and comparable values are placed in brackets underneath them. These values were determined by a method described in a former paper*. I do not venture to ascribe to them a higher importance than that of approximations merely, inasmuch as for deflections of the needle exceeding 40° the differences between the observed and calculated values become far too great to warrant correctness within a few degrees. The figures under z express in minutes the time from the beginning of the experiment until the junction reached its maximum temperature. The tension of the gases in the interior of the glass cylinder is given in millimetres under p; and, finally, the last column contains comparable values expressing the intensity of the thermal action on the junction.

* Pogg. *Ann.* Bd. clv. S. 98.

TABLE I.

	T.	*t*.	*τ*.	*z*.	*p*.	$\frac{100\tau}{t}$.
Dry air	19·8		0	0	760	
	56·0					
	47·7	27·9	50·5 (99·25)	22	—	356·6
Air-vacuum(approx.)	18·4		0	0	15	
	54·6					
	47·0	28·6	48·0 (88·5)	15	—	309·5
Hydrogen	22·5		0	0	760	
	57·5					
	50·5	28·0	57·8 (130·6)	17	—	466·4
Rarefied hydrogen...	23·0		0	0	5	
	58·0					
	52·1	29·1	53·0 (110·0)	14	—	378·0

Air as well as hydrogen, before being introduced into the apparatus, was passed slowly through a tube 40 centims. long, filled with well-dried calcium chloride; and a beaker filled with calcium chloride was placed in the glass cylinder.

The results of these experiments are, as far as hydrogen is concerned, the same as those obtained by Magnus, viz. that the denser hydrogen is more diathermanous than the rarefied. Air, however, shows the same property, the cause of which becomes clear on studying the course of the experiments.

After the greatest deflection of the needle had been reached, it remained almost constant for 30 minutes or more, although the temperature of the hot water continually decreased. The decreasing supply of heat from this source had therefore to be made up in some other way. By suddenly cooling the contents of the brass vessel by means of ice, the influence on the needle was perceptible only after the lapse of several minutes. Evidently the temperature of the junction had become more and more dependent on the thermal condition of the sides of the cylinder. Inasmuch as the conductivity of glass is not great, it is easily conceivable how the temperature of those parts of the cylinder at a distance from the heating vessel continued to rise, although the temperature of the water had already considerably decreased. Under these conditions the thermometer must have received numerous heat-rays from the sides of the cylinder, and upward currents of gases must have been produced whenever the glass cylinder was filled with gas.

The results of the experiment must therefore remain doubtful as long as no care is taken to prevent the heating of the walls of the vessel intended to receive the thermopile.

In the subsequent experiments, the annular space between the inner and outer glass cylinder was filled with water, at the temperature of the room, up to within 7 millims. of the bottom of the brass vessel.

The effect of this alteration became at once apparent: the deflections of the needle became less; and the maximum effect was more quickly attained. I give as illustration of this the following series of experiments:—

TABLE II.

	T.	t.	τ.	z.	p.	$\frac{100\tau}{t}$.
Dry air	10·9	—	0	0	739·5	
	38·3	—	—	—	—	
	34·0	23·1	20·5	12	—	88·7
Air-vacuum	12·8	—	0	0	1·5	
	41·5	—	—	—	—	
	37·1	24·3	31·0 (35·15)	6·5	—	144·6
Hydrogen-vacuum ..	11·8	—	0	0	734·3	
	40·5	—	—	—	—	
	38·4	26·6	38·0 (50·45)	7	—	190·0
Rarefied hydrogen..	12·6	—	0	0	1·5	
	41·0	—	—	—	—	
	36·9	24·3	36·0 (45·5)	6·5	—	187·2

After removing the strip of silver intended to serve as screen for the junction of the thermopile, the following figures, but slightly differing from the previous ones, were obtained:—

TABLE III.

	T.	t.	τ.	z.	p.	$\frac{100\tau}{t}$.
Dry air	11·5	—	0	0	745·5	
	40·3	—	—	—	—	
	35·1	23·6	21·5 (21·63)	9	—	91·6
Air-vacuum	12·1	—	0	0	1·5	
	39·8	—	—	—	—	
	34·5	22·3	32·0 (36·9)	11	—	165·5
Dry hydrogen	11·2	—	0	0	749·0	
	41·2	—	—	—	—	
	37·0	25·8	42·0 (62·6)	6	—	242·6
Hydrogen-vacuum ..	12·3	—	0	0	1·5	
	39·5	—	—	—	—	
	35·7	23·4	34·0 (41·2)	6	—	175·8

A comparison of the two Tables shows that the effects upon the junction were somewhat greater on the removal of the screen, but they did not alter essentially. Since the screen appeared thus superfluous, and might even have disturbed the uniformity of the experiments, it was henceforth emitted.

The propagation of heat in air, which at first had exceeded that in vacuum, upon cooling by water considerably fell below the latter. Now, since the thermal motion in strongly rarefied air could essentially be caused only by radiation, it follows that air of atmospheric density must exercise a considerable absorptive power on such rays as have proceeded from a source of moderate temperature. In the first experiments, when no cooling-water was used, this property of air must have been concealed by the upward currents conveying heat to the soldered junction. But the same disturbing influence must have manifested itself in the experiments with hydrogen, and favoured the passage of heat through this gas, independently of its supposed conductivity.

The last two series of experiments likewise show, notwithstanding the use of the cooling-water, an accelerated thermal motion in hydrogen, as Magnus had found, which led him to infer the metal-like conductivity of that gas. It was, however, remarkable (and this was noticed in several experiments the results of which closely agreed) that just when free circulation of the gas was most impeded, viz. when the screen was used, the difference between the passage of the heat on the one hand through dense hydrogen, on the other hand through rarefied hydrogen, was found to be least. But other circumstances led me to suppose that, even with the cooling water, currents were not entirely prevented during the experiments.

The return of the needle from maximum towards zero by no means corresponded to the decrease in the temperature of the water. Indeed, even upon suddenly reducing the latter to the temperature of the surrounding atmosphere, the needle remained for some time deflected. The diminished influence of the hot water, consequent on its gradual cooling, was therefore partially compensated for by the fact that the sides of the cylinder did not with proportionate rapidity yield up to the cooling-water the heat which they had received from the water in the brass vessel. It was, in fact, found after each experiment that the upper layer of the cooling-water had become appreciably warmer, though the difference at the height of the soldered junction was seldom more than one degree, frequently even less. I noticed, however, that even such small differences of temperature had an observable effect upon the needle; but these differences of temperature may have been somewhat greater on the inside of the glass cylinder.

As currents seemed unavoidable under these circumstances, more especially in the mobile hydrogen, and as thus there was sufficient ground to suppose that these currents were the only cause of the greater thermal motion of hydrogen, it appeared indispensable to maintain a constant change of the cooling-water. This was done by drawing off the water by means of a siphon from the upper part of the annular space, whilst at the same time cold water was introduced at the bottom. By this arrangement the temperature of the cooling-water was maintained so uniform that it did not change more than 0·1 to 0·2 degree in the course of an observation.

In addition to this, the soldered junction of the thermopile was lowered from 23 to 45 millims. below the bottom of the brass vessel; this distance was still some millimetres less than that Magnus had in his experiments. By this means as well as by the cooling-water, the possibility of the glass becoming warm down to the level of the soldered junction was considerably diminished.

The following figures were now obtained for dry hydrogen and air:—

Table IV.

	T.	t.	τ.	z.	p.	$\frac{100\tau}{t}$.
Hydrogen ...	11·0 46·0 39·6	28·6	11·5	8	760·0	40·2
Hydrogen ...	11·0 55·3 47·5	36·5	15·9	7	755·0	43·6
Air	11·0 52·0 45·3	34·3	7·5	7	744·5	21·8
Air	10·5 51·0 43·0	32·5	13·5	7	1·5	40·0
Air	9·4 60·0 51·3	41·9	16·5	7	1·5	41·5

On comparing, as exhibited by these figures, the relation of the thermal motions in hydrogen and in vacuum, an almost entire similarity is observed. Now the motion in vacuum is almost exclusively due to radiation. The conclusion seems therefore justified, *that hydrogen is as diathermanous to rays, emanating from a body heated by means of hot water, as a vacuum.*

True, what we speak of as a vacuum is not absolutely free from gas; when compared with a perfect vacuum the diathermancy of hydrogen may possibly be less. This seems even beyond doubt; for it would be impossible to raise the temperature of hydrogen if this gas did not possess any absorptive capacity for heat.

The preceding remarks, as already stated, are not meant to deny that hydrogen possesses a certain degree of thermal conductivity, but to show that this conductivity is too small to become distinctly apparent—*i. e.* beyond the limits of the errors of observation in the experiments performed by Magnus and repeated by myself.

The numerical results given in Magnus's paper* exhibit, therefore, not the differences in conductivity of the various gases, but in diathermancy, greatly affected though by disturbing influences. This is especially the case for air and hydrogen, the figures of which are too high in comparison with the average value found for vacuum. In this manner the supposition must have originated, that hydrogen possesses a conductivity similar to that of the metals.

Proceeding from this supposed property of hydrogen, Magnus thought he had found the key to the explanation of Grove's experiment, that a platinum wire, through which the electric current passes, loses its incandescence in hydrogen, though not in air. But this phenomenon is just as easily explained by the greater diathermancy of hydrogen than of air, more especially if we take into consideration its behaviour in vacuum, which Grove seems not to have noticed.

The greatest incandescence of the wire, *omnibus paribus*, takes place in vacuum; and the incandescence diminishes in a striking manner when air is admitted; on admission of hydrogen instead of air, the white incandescence sinks to a dull red heat.

The researches of Dulong and Petit on the laws of cooling bodies† have established the fact that a heated body cools more rapidly in gas than in vacuum, and that this rapidity varies for different gases. In so mobile a medium as hydrogen, a very rapid current may be formed without an essential diminution in the loss of heat by radiation. The conditions for rapid thermal motion are thus most favourable. True, for atmospheric air the convection may also be great; but the loss by radiation is diminished; the rapidity of thermal motion must therefore be less than in hydrogen. Inasmuch as the diathermancy of the air is less than that of hydrogen, this would of itself explain

* Phil. Mag. vol. xxii. p. 10.

† *Ann. Chim. Phys.* t. vii. 1817.

the more rapid cooling of a body in the latter medium, even if the conductivity of both gases were the same.

According to the results of the fourth series of experiments, the air impedes the passage of heat-rays in a striking manner. The air employed had been, as stated, carefully dried ; nevertheless about half of the incident rays were absorbed by the layer of air between the bottom of the heating-vessel and the soldered junction of the thermopile. As this result was in contradiction to the experience hitherto collected, further observations were required in order to confirm it.

To increase the deflection of the needle, the upper surface of the soldered junction was covered with lampblack ; by this means the desired result was attained.

In the following Tables, T denotes the temperature of the water in the brass cylinder at the beginning of an experiment, T′ the temperature of the water when the needle had reached its maximum deflection τ. The differences of temperature at which τ was obtained are given under t, and $T-t$ is therefore the temperature in the brass cylinder before the introduction of the hot water. Finally, the figures under z' give the duration of each experiment from the time when the hot water was introduced, and column p represents the interior tensions.

TABLE V.

Diathermancy of Dry Air at different Densities.

T.	T′.	t.	τ.	z'.	p millims.	$\frac{100\tau}{t}$.
41·8	36·3	29·1	12·0	6	1·5	41·2
51·0	43·0	32·5	13·5	7	1·5	41·5
54·0	46·5	38·2	17·6	4	1·5	46·0
63·0	55·0	47·4	20·2	5	1·5	42·6
84·0	70·3	63·2	27·1 (29·0)	5	1·5	45·9
48·0	41·3	31·1	6·0	7	748·0	19·3
52·0	45·3	34·3	7·5	7	744·0	21·8
85·0	70·1	61·1	13·0	5	748·0	21·2
81·0	73·2	65·7	13·5	6	750·4	20·5
67·3	58·8	50·8	12·7	7	520·6	25·0
82·4	67·5	60·3	16·4	7	414·5	27·2
64·0	54·5	46·5	13·5	7	254·7	29·0
62·0	51·0	43·2	16·0	7	108·0	37·0
64·0	53·4	46·9	18·8	5	12·1	40·1
66·0	54·5	48·0	10·0	7·5	747·3	20·8

The first five experiments in the above Table, in which the thermal motion could have been caused by radiation alone, furnish a very convenient test of the correctness of the method

of calculation taken as the basis of my experiments. The starting-point of this calculation is the assumption that the maximum deflection is in every case proportional to the difference of temperature t. If this were correct within the range of the temperatures selected, the first five figures in the last column ought to be equal, or nearly so. A more careful consideration of my experiments, however, leads me to the conclusion that the differences there apparent do not arise solely from errors of observation, but chiefly from the fact of its being impossible, notwithstanding all precautions, to overcome the influence of heat from the sides of the glass cylinder. The differences between the numbers found and their average value, $\frac{100\tau}{t}=43{\cdot}4$, however, are much too small to leave the main question doubtful.

To show the difficulties of maintaining the initial temperatures of the glass cylinder, I give here an experiment in full:—

Table VI.

T.	τ.	z.	T′.
		h	
7·1	0	9·55	7·34
84·0	23·0	9·56	7·34
74·0	26·5	9·58	7·34
71·4	27·0	9·59	7·34
70·3	27·1	9·60	7·34
68·8	27·0	9·61	7·34
68·0	27·0	9·62	7·35
66·4	26·7	9·63	7·35
64·5	26·0	9·65	7·33

The figures of the first three columns require no further explanation; those in the fourth column, under T′, give the temperatures of the cooling-water at the height of the junction—*i. e.* 38 millims. under the surface of the water. Here, as is apparent, the temperature could be kept very uniform by means of the regular flow of the water from the surface. But it was impossible to avoid a gradual increase of temperature above that point and towards the inside of the vessel. This is shown by the still rather slow return of the needle after it reached the maximum. It is clear that the maximum was thus somewhat altered, though to a very trifling degree, which in some cases, however, may not have been exactly proportional to the differences of temperature. But, as already stated, the main question at issue, that of the great absorptive power of air for rays of low temperatures could only slightly have been affected thereby.

The average of five experiments gives for air of atmospheric density the number $\frac{100\,\tau}{t} = 20{\cdot}7$, whilst for a vacuum of only 1·5 millim. tension the average value was $\frac{100\,\tau}{t} = 43{\cdot}4$. Thus half of the rays of low refrangibility entering dry air of atmospheric density are absorbed by those layers which are nearest the sources of heat.

With decreasing density the diathermancy increases. But the experiments 9 to 15 of the Table show that the increase is not inversely proportional to the tension of the air, but takes place much more rapidly, so that for a tension of 100 millims. the diathermancy approaches very near that of a vacuum.

The effect upon the junction of the thermopile was next determined when the source of heat was at a greater distance from it. This was done in order to determine whether the absorption took place immediately upon the entrance of the rays, or whether the lower layer of air likewise absorbed part of the rays.

The connecting wires of the thermopile were therefore shortened so that the soldered junction was 100 millims. below the brass plate. At this depth there was no rise of temperature perceptible on the outer surface of the glass cylinder.

The results of the experiments carried out in this manner did not answer my expectations. The deflections of the needle diminished to such a degree that, even under the most favourable circumstances, they scarcely ever exceeded 4° ; the absorptive power of air, instead of proportionately increasing, as I had supposed, seemed to decrease from the 50 per cent. previously observed to 20 and even 15 per cent.

To obtain greater deflections of the needle, the lower side of the bottom of the brass vessel, which had hitherto remained metallic, was also covered with lampblack, but without favourable result. The deflections increased but feebly, though the radiating-power of the source of heat must have been six or seven times greater than previously ; on removing the cooling-water, however, the deflections increased to such a degree as to become useless.

The soldered junction of the thermopile, when placed 100 millims. below the bottom of the brass cylinder, was thus nearly entirely withdrawn from the influence of the source of heat, and was dependent only upon the temperature of the cooling water. This ought not, of course, to have affected the relation of the forces which deflect the needle, according as the space was exhausted or filled with air, if in both cases the influence of the cooling-water had remained proportional to the

real heating-effect of the brass vessel upon the cooling-water. This, however, was evidently not the case.

From the small deflections of the needle, varying within 2 and 5, it was evident that the temperature of the junction, even had it reached its maximum, could not be very different from that of the surrounding air. Inasmuch as the air itself absorbed some of the incident rays, its temperature above the junction must consequently have been gradually rising. Scarcely any cooling of the junction by upward currents was observable. As soon as equilibrium was restored between the influx and loss of heat, the loss must have been occasioned, in vacuum as well as in air, chiefly by radiation. But the results of the preceding experiments show that the loss by radiation is greater in vacuum than in air. The soldered junction retains in the latter case, therefore, a comparatively higher temperature. In other words, the same causes which retard the influx of heat by radiation lessen, on the other hand, the loss. Thus the diathermancy of air appears greater than it is in reality.

By wrapping the junction in paper this source of error was diminished—and upon covering the interior of the cylinder with double cardboard, nearly disappeared.

The numbers obtained when this protection against the disturbing influence of the cooling-water was used are as follows:—

Table VII.

T.	T'.	t_s	σ.	z'.	p, millims.	$\frac{100\,\tau}{t}$.
Dry air.						
66·0	46·5	41·0	7·0	5	755·0	17·10
65·8	49·0	44·0	7·5	5	753·0	17·04
60·3	44·0	39·4	11·5	5	4·8	30·00
63·0	46·0	40·6	11·8	5	2·5	29·00
Dry hydrogen.						
70·0	46·5	40·6	12·3	7·0	755·5	30·3
67·0	45·8	39·7	11·7	6·5	755·5	29·5

The absorptive power of the dry air is almost similar to that formerly obtained when the junction was nearer the source of heat. The experiments with hydrogen, quoted in Table VII., show the close agreement of its diathermancy with that of a vacuum.

The absorptive power of air for greater distances from the

source of heat, I have not yet been able experimentally to determine. Glass cylinders of larger diameter would be necessary in order to have the cooling-water more distant from the junction of the thermopile. These experiments, though unsuccessful, have, I think, shown why the results obtained by other observers, whose names alone are sufficient guarantees for the correctness of their statements, differ so very widely from those obtained by me.

According to the first observations made by Magnus, dry air absorbs 18 per cent. of the heat-rays proceeding from a dark source*. But it has already been pointed out that sources of error sufficient to account for such differences were not taken into consideration in his method. His thermometer, particularly, was not sufficiently protected from currents of warm air.

Magnus himself does not seem to have placed much confidence in those experiments, as far as they had reference to the diathermancy of different gases; for in a second series of experiments †, undertaken with the view of investigating the diathermancy of gases, his apparatus was essentially altered: for the mercury thermometer, as described in his memoir, a thermoelectric pile was substituted. This was placed in a glass cylinder 175 millims. in height by 100 millims. in width, and surrounded by water of constant temperature. The source of heat was at least 200 millims. above the face of the pile; and the rays before reaching the face had to pass through a narrow channel of only 24 millims. width. With this apparatus Magnus found that the air absorbed only 11 per cent. of the incident rays.

Here there could be no possibility of a disturbance from air-currents; but other difficulties presented themselves. The thermopile, whose bars were only 30 millims. long, was wholly within the vessel for the reception of the gases; one face was turned towards the source of heat; the other was fixed to the plate of an air-pump by means of a cork, into which the lower end of the cylindrical casing penetrated for a short distance. This arrangement prevented, or at least impeded, a free circulation of the gases around the lower face of the pile.

It is probable that, as the experiment lasted several minutes, the heat received by the blackened front face of the pile was soon propagated to the lower face (where, as already stated, the elimination of heat was greatly impeded), and very soon raised its temperature above that of the surrounding medium.

In consequence of this, the difference in temperature of the

* Phil. Mag. vol. xxii. p. 10. † Ibid. p. 95.

two faces of the pile became incompletely developed, the deflections of the needle being indeed greatest in those cases in which the rays passed most directly to the pile, *i. e.* when they traversed a vacuum or hydrogen. And such behaviour is clearly shown in the experiments.

A still more important source of error lay in the considerable distance of the source of heat from the thermopile as compared with the small diameter of the glass cylinder.

Almost simultaneously with Magnus, Tyndall published a comprehensive memoir on the diathermancy of gases and vapours *. His method differs essentially from that first adopted by Magnus, in that the rays had to pass through a polished plate of rock-salt before they reached the vessel containing the gas under investigation. This vessel consisted of a horizontally placed metal tube 4 feet in length, polished internally and hermetically closed at both ends by plates of rock-salt. The heat-rays emanating from a Leslie's cube at a distance of 8 inches, after passing through the air, entered the tube through one of the rock-salt plates, issued again by the second, and, having traversed a second layer of air, fell upon the conical reflector of a thermopile.

By this method all the heat-rays for which air is athermanous were evidently absorbed ; and hence those entering the tube would pass through it unhindered when the tube was filled with dry air. This would also be the case for the chief constituents of air, oxygen and nitrogen, as well as for hydrogen or even a vacuum, since these media allow all rays to pass. In this way the result would be obtained, that the four gases exhibit the same behaviour as a vacuum towards heat-rays from a dark source.

In a subsequent series of experiments, Tyndall employed a small chamber fixed air-tight onto one of the rock-salt plates, its opposite sides being similarly closed by one of the faces of the cube. During the experiment the chamber was exhausted ; so that the heat-rays, before entering the tube, could not suffer any loss except by their passing through the rock-salt. Nevertheless the results differed very little from the preceding ones. A small but not constant fraction of the incident rays (according to Tyndall about 0·33 per cent.) was lost. Such a result was indeed to be expected ; for since the rays had still to traverse a layer of air before reaching the thermopile, only those rays could arrive there for which air is diathermanous. But the rock-salt also may have retained some of the incident rays. Melloni had, it is true, pronounced rock-salt to be completely

* Phil. Mag. [IV.] vol. xxii. p. 169.

diathermanous; and it was perfectly justifiable to trust such an authority. But Melloni was not aware that air absorbs a considerable proportion of heat-rays: he, indeed, regarded it as diathermanous, because he had observed that rays, after once entering air, lose nothing after traversing a distance of several metres. He never compared the diathermancy of air with that of a vacuum, nor did he try to send rays from a vacuum into rock-salt. Thus it might easily occur that rock-salt, though it allowed all rays coming from air to pass, nevertheless absorbed a portion of rays issuing from their source directly through the vacuum.

To solve this question experimentally, my apparatus required only a slight alteration. The soldered junction of the thermopile, which was at 45 millims. distance below the bottom of the brass vessel, was surrounded with a jacket of thin sheet brass; this jacket, open at both ends, rested on the plate of the air-pump, and was provided at its upper end, which was about 20 millims. above the level of the soldered junction, with a circular opening about 44 millims. wide, in which a plate of clear rock-salt could be inserted. This plate, 3 millims. thick, had been cut and carefully polished by M. Steeg in Homburg v. d. H.

The following experiments were made with air at 4·2 millims. tension:—

Table VIII.

Opening.	T.	T'.	t.	τ.	z.	$\frac{100\,\tau}{t}$.
Free	70·0	47·0	40·7	20·3	7	50·0
	67·0	45·0	38·4	20·2	7	52·6
Covered with rock-salt	89·0	58·0	51·3	17·8	7	34·9
	70·0	47·5	41·5	10·9	7	26·3
	32·0	23·0	17·0	5·1	7	30·0

These experiments confirm the hypothesis previously stated. They show that less than 60 per cent. of the rays from the hot-water vessel pass through a plate of clear rock-salt only 3 millims. in thickness. A very considerable proportion of these rays is thus retained by the rock-salt.

The question still remained, how far air and rock-salt agree in their thermal colours. The following series of experiments give us a solution of this problem. In every case the circular opening was covered with the rock-salt plate, and the interior of the glass cylinder was lined with pasteboard.

Table IX.

T.	T′.	t.	τ.	z'.	p, millims.	$\frac{100\,\tau}{t}$.
49·0	36·0	30·3	23·9 (24·5)	14	755	80·9
55·0	39·0	33·9	27·1 (29·0)	14	745	85·5
57·0	39·0	35·0	27·0 (28·9)	14	745	82·6
42·3	25·7	25·7	24·6 (25·5)	14	9·2	97·7
56·0	32·0	32·0	30·0 (33·6)	14	7·8	105·0
56·0	31·3	31·3	28·1 (30·5)	14	7·7	97·4

In the first three experiments the air in the glass cylinder was of atmospheric density, in the last three it was greatly rarefied. Of about 100 rays which passed through the rarefied space and the rock-salt, only about 83 were transmitted through the denser air.

The thermal colours of the two substances are not perfectly alike, but sufficiently similar to explain the phenomena observed by Tyndall.

Tyndall determined the absorptive capacity of dry air from the very small alteration caused by filling the previously exhausted tube of 4 feet length with dry air. After what has been stated it will not be surprising that other gases, such as moist air and olefiant gas, possessing other thermal colours, when substituted for dry air in the tube, produced greatly different effects upon the galvanometer. But such differences do not prove a greater absorptive power of the respective gases, as Tyndall supposed, but, in the first instance, a difference only in their thermal colours.

On comparing the small effect of dry air upon the needle with the greater one produced by moist air, as resulting from his mode of observation, Tyndall arrived at the remarkable conclusion that the thermal absorption of the latter is from 20 to 40 times as great as that of the former. This conclusion was called in question by Magnus, who had found in his experiments with dry and moist air, when not using a plate of rock-salt, that the difference in their absorptive powers for rays of the temperature of boiling water is very small, though that of moist air is somewhat the greater. Thus originated the well-known controversy between the two scientific men—a controversy which excited all the more interest, inasmuch as both

were regarded as equally reliable and acute observers, and yet the results were so widely different.

My own observations on the diathermancy of moist air agree pretty closely with those of Magnus. Unfortunately, the season of the year prevented the application of tensions above a temperature of 13°; I purpose to continue my experiments in this direction under more favourable conditions of temperature.

For the experiments which hitherto have been made, the above-described apparatus with the glass cylinder was employed. The soldered junction was 45 millims. below the bottom of the brass vessel. The numbers obtained are tabulated with those for carbonic acid and for hydrogen; those for the latter are the results of a repeated examination.

TABLE X.

T.	T'.	t.	τ.	z'.	p, millims.	$\frac{100\,\tau}{t}$.
			Hydrogen, dry.			
62·5	51·5	40·5	18·4	7	1·5	45·4
47·0	38·5	32·4	15·0	7	1·5	46·3
39·0	32·5	26·7	12·5	0	759·0	46·8
			Carbonic Acid, dry.			
62·0	53·0	43·2	8·3	5	750·0	19·2
82·0	66·5	58·0	11·0	7	750·0	19·0
			Moist Air.			
81·0	69·0	60·2	23·1 (23·5)	6	8·2 (9°)	39·0
85·0	73·5	57·15	19·4	6	12·9 (12°)	34·0
87·0	79·0	62·0	12·5	7	756·6 (10°·9)	20·1
70·0	55·7	44·2	8·7	6·5	756·6 (10°·7)	19·7
86·0	72·0	59·0	11·5	6	756·6 (13°·7)	19·5

The numbers of the last column are throughout comparable with the corresponding ones obtained in preceding experiments with a distance of 45 millims. between the brass plate and the junction, and according to which, for dry air of atmospheric density, $\frac{100\,\tau}{t} = 20{\cdot}7$, for vacuum $\frac{100\,\tau}{t} = 43{\cdot}4$. The radiating brass bottom was clean and polished; the soldered junction was covered with lampblack, as in the experiments quoted in Table V. The carbonic acid, prepared from sodium carbonate by sulphuric acid, was dried over calcium chloride.

To fill the glass cylinder with aqueous vapour, a small vessel of water was placed within it; near it a thermometer was hung, the readings of which are given in brackets in the last column but one.

The first two experiments with moist air were made in a space as highly rarefied as was attainable by means of the air-pump. The manometric numbers indicate therefore the pressure of a mixture of air and water-vapour, in which that of the former did not exceed 1·5 millim. After the termination of these experiments, air of 75·7 millims. barometric pressure was allowed to enter the space already saturated with vapour. The amount of vapour had to be determined from the temperature indicated by the thermometer.

It appeared of particular interest to investigate olefiant gas according to this method—partly because its specific gravity so closely approximates to that of air, and partly because, notwithstanding the large proportion of hydrogen it contains, it was found both by Magnus and Tyndall to absorb more of the heat-rays than air.

In has been pointed out that the basis of Tyndall's comparisons was not reliable; and it is probable that in Magnus's experiments conditions obtained such as led him to find the diathermancy of hydrogen smaller than that of the air.

On the other hand, Dulong and Petit, in their extensive researches on the laws of cooling *, compared the rapidity with which a thermometer cooled in contact with air, hydrogen, carbonic acid, and olefiant gas successively (all four gases taken at the same pressure), and found that the heated body cools most rapidly in hydrogen, and next in olefiant gas. Considering that equal volumes of air and of olefiant gas have almost the same weight, the idea naturally presents itself of supposing that the above-mentioned behaviour is due to the fact of the diathermancy of olefiant gas being greater than that of air and of carbonic acid.

The gas used in my experiments was prepared from a mixture of sulphuric acid and alcohol by Messrs. H. W. Will and A. Winther, assistants in the chemical laboratory of this University. It contained a trace of ether, and might, whilst being introduced into the apparatus, have taken up a small quantity of air, though the cylinder was repeatedly filled with fresh quantities of the gas before the experiment was begun. The numbers of the following Table cannot be directly compared with those of V. and X., because in those two series the junction was covered with lampblack, and the bottom of the metal cylinder was clean and bright, whilst in the present experi-

* *Ann. Chim. Phys.* t. vii. p. 351.

ments the reverse was the case. Moreover the distance was less than 45 millims., which gave greater deflections. For the sake of comparison, the results of experiments repeated with dry air and the vacuum are also given.

TABLE XI.

(Each experiment lasted six minutes.)

	T.	T′.	t.	τ.	p, millims.	$\frac{100\,\tau}{T}$.
Dry air	63·0	60·0	42·2	28·0 (30·4)	5	72·03
	60·0	51·0	43·6	15·2	738·5	34·86
Dry olefiant gas	59·0	48·0	42·5	17·8	742·6	41·9
	58·0	47·0	40·5	16·2	656·0	40·0

From these experiments the diathermancy of olefiant gas appears somewhat higher than that of air. True, I cannot warrant the purity of the gas; but I believe that any possible admixtures must have tended rather to increase than to diminish the absorption.

The diathermancy of a hydrogen-vacuum of 1·5 millim. tension may be considered as very closely approximating to that of an absolute vacuum. The comparable average value of the numbers for a hydrogen-vacuum gave $\frac{100\,\tau}{t}=45{\cdot}4$. Dividing the values of the other gases by this number, and multiplying the quotient by 100, the following ratios are obtained:—

Name of the gas.	Tension, in millims.	Diather-mancy.	Absorp-tion.
Hydrogen, dry	1·5	100 0	0
	750–760	102·0	0
Air, dry	750–760	45·6	54·4
,,	520·6	54·5	45·5
,,	414·5	60·0	40·0
,,	254·5	63·0	37·0
,,	108·0	80·4	19 6
,,	12·1	87·5	12·5
,,	1·5	95·6	4·6
Air-vacuum, moist at 12° C.	12·9	74·2	25·8
Air, saturated with vapour at 12° C.	756·6	43·2	56·8
Carbonic acid, dry	750·0	42·1	57·9
Olefiant gas	750·0	53·6	47·4

Hydrogen at ordinary pressure always gave a somewhat higher number than a vacuum; so that I cannot suppose that the difference is due merely to errors of observation. Nevertheless I do not regard this as a proof of conduction, which would re-

quire to propagate itself to a distance of 100 millims. in the short interval of five minutes ; I am rather inclined to ascribe this to the very great mobility of the hydrogen molecules.

Water-vapour in vacuum, however small the quantity, absorbs a considerable amount of heat, in any case more than air of the same tension; but in air of atmospheric pressure this preponderance is not very striking ; in other words, rays which are not absorbed by dry air pass to a great extent also through moist air.

Other experimenters have taken more or less active part in the controversy on the magnitude of the absorptive power of aqueous vapour for rays of low refrangibility. The researches of H. Wild* are particularly deserving of attention.

Wild studied carefully Tyndall's method, as well as that of Magnus. The measurements, however, which he communicated were obtained with an apparatus resembling that of Tyndall† without rock-salt plates. His somewhat altered arrangement is well adapted for exhibiting to a large audience the fact that moist air absorbs rays from a dark source better than dry : but the real point at issue is not touched at all by this fact; for Magnus himself had repeatedly acknowledged the higher absorptive power of moist air, denying only that this was from 15 to 40 times as great as that of dry air. In this respect Wild's experiments give as little information as those previously made by Tyndall ; for in both cases the rays, before entering the spaces saturated with moisture and reaching the thermopile, had passed for a certain distance through the air of the room—and consequently had lost the rays capable of absorption by air, without being able to affect the thermomultiplier.

As already stated, Wild also submitted Magnus's process to an experimental investigation ; but in consequence of his preconceived notion that the absorptive power of air was very small, he failed to draw the right conclusions from indications in a contrary sense which his own experiments offered‡.

One circumstance in Wild's memoir produced doubts in my mind when first reading it. He assumes that the absorption is proportional to the thickness of the absorbing layer, and concludes from this that Magnus had obtained smaller values than Tyndall, to a certain extent, because the distance of the thermopile from the source of heat had been too short in his experiments.

It is quite justifiable to assume that, within certain limits,

* Phil. Mag. [IV.] vol. xxxii. p. 241.
† Ibid. vol. xxiv. p. 270; also vol. xxvi. p. 21.
‡ Ibid. vol. xxxii. p. 254.

the absorption of a layer of gas increases with the thickness as with its density; but for air and aqueous vapour these limits must be drawn closely.

Melloni had shown by experiments * that a layer of air of 5–6 metres thickness exercises no perceptible absorption on rays proceeding from a body heated to 100° C. Tyndall and Wild have accepted this fact, and indeed based upon it the disposition of their apparatus.

But Melloni's experiments in this direction were performed in an open space. The air employed, like that of any space to which the atmosphere has free access, must have contained aqueous vapour, though this is not expressly mentioned. If the absorption of moist air increased for such great distances, and as considerably as Wild supposed, the experiments of Melloni necessarily would have led to a different result. I conclude from this that the absorption of both, dry as well as moist air, very rapidly diminishes, and must soon become imperceptible in a layer the thickness of which may be left out of consideration when compared with the magnitude of the distance at which Melloni had carried out the first of his comparative experiments.

The experimental part of the present investigation had been completed when my attention was directed to the analogous researches of Hoorweg †. The observations of Magnus and Tyndall are here elaborately and impartially compared, and critically elucidated, chiefly with regard to the absorptive capacity of moist air. Hoorweg's own experiments led him finally to the same result which Magnus had attained, and at which I, too, had arrived by my experiments performed in a perfectly different manner, viz. that the absorption of moist air differs but little from that of dry. Hoorweg's researches, however, extend only to those rays which, before examination, had been deprived of the portion for which air is athermanous. The disproportion of Tyndall's numbers therefore naturally escaped him.

In contradiction to Melloni's experience, previously mentioned, Hoorweg finds that the absorption in moist air increases with the length of the layer. This result of his experiments, however, is open to objections. He filled the space between the source of heat and the thermopile with moisture by introducing air which had been forced through a box containing moistened fragments of quartz. It is possible that in this way, along with aqueous vapour, finely divided particles of liquid water had been carried along into the space.

I pass over the conclusions regarding the thermal conditions

* *Thermochrose*, S. 136. † Pogg. *Ann.* Bd. civ. S. 385.

of the earth's surface which might be drawn from the great absorptive power of the air for rays of low refrangibility, such as are largely present in the solar rays, and conclude this paper with a short summary of the chief results of my experiments.

The thermal conductivity of hydrogen and of other gases is far too small to admit of its being proved by the method Magnus adopted. The assumption that the conductivity of hydrogen is similar to that of the metals, if by this statement any thing more is meant than that hydrogen, like solid and liquid bodies, is capable of transmitting heat from molecule to molecule, is therefore not justified.

On the other hand, hydrogen possesses a diathermancy closely approaching that of a vacuum.

Dry air absorbs from 50 to 60 per cent. of the rays of heat which it receives from a source heated to the boiling-point of water.

The absorptive power of moist air surpasses that of dry air by a trifling percentage, but by no means to such a degree as hitherto had been assumed by several physicists.

Rock-salt is not absolutely diathermanous for the so-called dark rays of heat; its thermal colour rather resembles that of dry air.

Giessen, March 30, 1876.

LVI. *On the Penetration of Heat across Layers of Gas.* *By* G. Johnstone Stoney, *M.A., F.R.S., &c., Secretary Royal Dublin Society**.

Part I. *Theory.*

1. HEAT will pass between bodies at different temperatures by direct contact, by radiation and absorption, or by contact with a fluid and convection through it. That heat may be transported in these several ways has long been known; and the laws of the transfer have been made the subject of repeated and careful investigation by experiment and by the deductive method. And last year two papers† were published by the author of the present memoir, in which it was shown that heat will also escape, under new conditions, across a Crookes's layer, if the layer be restricted in width. In those papers the mechanical actions that arise, and upon which Mr. Crookes had made many experiments, were made the subject of study; and the present communication aims at

* From the Scientific Transactions of the Royal Dublin Society for 1877. Communicated by the Author.

† See Phil. Mag. for March and April 1876.

extending the investigation to the second branch of the subject, viz. the transfer of heat which accompanies those mechanical actions.

2. When gas is in contact with a body A at a different temperature from itself, it is a familiar fact that convection currents rapidly set in. The first step of the process is the almost instantaneous formation of that layer which I have called Crookes's layer—a layer of the gas of varying density and temperature, being on one side at the temperature of the body A, and on the other side at the temperature of the surrounding gas. It is because this layer has a different density from the rest of the gas, and because of the attraction of the earth, that those streams set in which are called convection currents; and accordingly, if the experiment could be made at a station where there is no gravity, these convection currents would not arise, although the Crookes's layer would then also be fully developed. It will be convenient to inquire first what will occur under these simplified conditions, and afterwards to take into consideration whether any modification has to be made to allow for the effect of the neighbouring earth. To give to the problem definiteness and the utmost simplicity, I will suppose that a body A at temperature θ_1 presents a large flat surface to an atmosphere of gas which is at a lower temperature θ_2, and exposed everywhere to a constant pressure, but which is uninfluenced by gravity. Let us further regard this gas as a perfect non-conductor of heat.

3. If the excess of temperature is supposed to be *suddenly* imparted to A, there will be a brief interval of adjustment within the gas, after which the condition of the gas will settle down into the state in which the Crookes's layer will have been fully formed. The Crookes's layer in this case will obviously consist of a flat stratum of the gas in contact with the hot surface of A; and within this stratum the temperature will gradually decrease from within outwards, from θ_1, the temperature of A, down to θ_2, the temperature of the surrounding gas. This gradual falling-off of the temperature implies a corresponding gradual augmentation of the density, since we have supposed the gas to be everywhere subjected to the same pressure. If the gas *could** admit of the formation of a *complete* Crookes's layer, then we know, from the familiar experiments which show gases to be bad conductors of heat, that after the brief interval of adjustment a permanent state would ensue, in which there would be no further change of density, or motion of heat except by radiation. Accordingly, if an isothermal surface be now drawn within the layer

* See page 427, the last paragraph of section 4.

(which, in the simple case we have supposed, will be a plane parallel to A), there will fly the same number of molecules per second in both directions, across an element δS of this surface, the momentum of the two processions which pass through δS in a second will be the same, and their kinetic energy also will be the same. Their number will be the same; for otherwise the density would be still undergoing change, and we have supposed that the period of adjustment is over. Their momentum will be the same, because the pressure is everywhere constant; and their kinetic energy is the same, because there is no transfer of heat across S.

4. Hence the change of temperature and density in passing along δx, an element of the normal to δS, must be such as to secure these three conditions. In investigating the law of this variation, we have to take into account:—

P, the pressure everywhere through the gas;
θ, the temperature (measured from absolute zero) on the isothermal surface S;
ρ, the density of the gas on the isothermal surface S;
x, the distance of S from A; and
G, a quantity which changes from one gas to another, but is almost constant in each gas, within a wide range of temperature and pressure.

When the gas and its tension are given, G and P are constants; and ρ is a known function of G, P, and θ. Hence only two of the foregoing quantities are independent—suppose θ and x, instead of which we may use $\frac{dx}{d\theta}$ and θ. It is easy to see, by taking particular instances, that $\frac{dx}{d\theta}$ and θ will remain independent of one another, if only two of the conditions in § 3 need to be fulfilled; but if all three have to be fulfilled, we find by experiment that a definite Crookes's layer is formed, and that, therefore, in each gas and at each pressure $\frac{dx}{d\theta}$ is a definite function of θ. In other words,

$$\frac{dx}{d\theta} = \psi(\theta, \mathrm{G}, \mathrm{P}), \quad . \quad . \quad . \quad . \quad . \quad (\alpha)$$

in which G and P are constants. This furnishes by integration an equation of the form

$$x = \text{const.} + \phi(\theta, \mathrm{G}, \mathrm{P}), \quad . \quad . \quad . \quad . \quad (\beta)$$

which represents the law by which the temperature must change across the layer. What we learn from this investigation is, that, besides the uniform distribution of a gas with the

same temperature everywhere, there is one other permanent distribution possible (except at the limits), and perhaps only one—that in it there is, for each gas and at each tension, a definite gradient of temperature, with its accompanying equally definite gradient of density in the opposite direction. These results might have been arrived at in another way, viz. by a consideration of the effects of the intermolecular encounters.

Another case in which the three conditions will be fulfilled is the familiar one of a *uniform* medium, in which case

$$\frac{d\theta}{dx}=0, \text{ or } \theta=\text{const.} \quad . \quad . \quad . \quad . \quad (\gamma)$$

But if there is a transition from one of these distributions to the other, as there must be where the Crookes's layer is in contact with the rest of the gas, there will be an interval of compromise, in which the three conditions are not strictly fulfilled. Similarly, they cannot be fulfilled where the Crookes's layer adjoins the hot body A. Hence there must, in the cases that really arise, be some escape of heat, which may be small, but cannot vanish, because discontinuity is impossible, since the length of the mean path of a molecule between its encounters with other molecules is finite. Hence, also, the values of the temperature at different depths within the Crookes's layer will differ by small amounts from those assigned to it by equation (β). It will appear, however, from the next paragraph, that the rate of cooling arising from these imperfections will be very slow*; and although the heat that passes would doubtless accumulate and ultimately become considerable if there were no gravity, its presence will be inappreciable in most of the experiments we can make, where the portion of gas in which the Crookes's layer is formed is being constantly renewed by convection currents.

5. We have hitherto supposed that the atmosphere of gas was of sufficient extent to allow the whole of the Crookes's layer to come into existence; but we shall have entirely new conditions if a body B at temperature θ_2, which for simplicity we may suppose to have a large flat surface, is placed parallel to A at a distance less than the thickness of an unrestricted Crookes's layer. In this case a *compressed*† Crookes's layer will come into existence, in which, as explained in § 16 of my former papers, the density of the gas must be everywhere

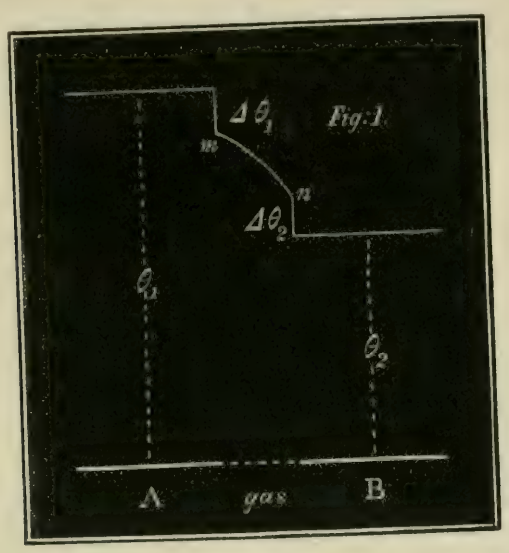
* For, the Crookes's layer being in this case almost complete, the values of $\Delta\theta_1$ and $\Delta\theta_2$ (see § 5) will be exceedingly small.

† *I. e.* confined between a heater and a cooler, against which the layer of gas expends its Crookes's stress. In withstanding this stress the heater and cooler compress the layer. A compressed Crookes's layer might also be called a layer of polarized gas.

greater than at the same distances from A in the complete Crookes's layer, to preserve the lateral pressure unchanged. Through each element δS of an isothermal surface the molecules will still travel in equal numbers inwards and outwards, because when the adjustment is once over, the density of the gas will not anywhere undergo further change ; but the molecules making their way outwards (*i. e.* from A towards B) will, on the whole, be swifter than those tending inwards, because there should be a *complete* Crookes's layer to enable the swifter class of molecules rebounding from A to keep back the whole of the slower kind which constantly tend to crowd in (see Phil. Mag. April 1876, p. 308, §§ 15, 16, and 17). Accordingly, if the molecules at any one moment within an element of volume be considered, the portion of them which form a procession travelling inwards will now be found more numerous than those advancing outwards, and at the same time so much slower that the momentum in the two directions is the same ; in other words, there is no molar motion of the gas, nothing in the nature of a wind. But that there is a continual transfer of kinetic energy from A to B across the intervening gas is evident, because members of the procession of colder molecules crowding up to A will cause the temperature $\theta_1 - \Delta\theta_1$ of the inner surface of the Crookes's layer to be lower than θ_1, the temperature of A ; while, at the same time, the members of the swift procession which reach B will cause $\theta_2 + \Delta\theta_2$, the temperature of the outside surface of the Crookes's layer, to be warmer than θ_2, the temperature of B. The Crookes's layer, accordingly, must acquire heat by its contact with A, and impart heat where in contact with B ; and as adjustments within the layer are made with a speed comparable with the velocity of sound in the gas, it is possible to arrange experiments in which the differences of temperature $\Delta\theta_1$ and $\Delta\theta_2$ shall have any amounts from 0—when the interval between A and B equals or exceeds the width of an unrestricted Crookes's layer, —up to values bordering upon $\frac{1}{2}(\theta_1 - \theta_2)$—which, in the cases where the temperatures θ_1 and θ_2 are not far asunder, is close to the limiting value produced by diminishing the interval between A and B, or by attenuating the gas.

Accordingly, if the variations of temperature were plotted down on a diagram, the ordinates representing temperatures, and the abscissas distances measured perpendicularly to the isothermal surfaces within the gas, we should obtain a figure something like that on next page. It is moreover manifest that the curve $m\,n$, representing the variations of temperature across the compressed or polarized Crookes's layer, will approximate more and more to a horizontal line the greater the tenuity of the gas.

6. Some idea will be formed of the quantity of heat which will pass from A to B by the process here described, and for which I would suggest the name *penetration*, by forming an expression which aims at roughly representing the quantity of



heat absorbed by the gas per second from a square centimetre of A. One such expression is approximately*

$$\frac{dQ}{dt} = V\sigma\rho_1 \frac{\Delta\theta_1}{\theta_1}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (\delta)$$

in which V is the velocity with which the adjustment is made, σ the heat which would raise a gramme of the gas one degree in temperature, and ρ_1 the density (referred to water) of the gas where it is in contact with A.

To get the loss by penetration per second from the whole surface of the cooling body, we have to find the value of the integral $\int \frac{dQ}{dt} dA$, dA being an element of the surface of the cooling body, and $\frac{dQ}{dt}$ having the value assigned to it above. If the surface is everywhere equally exposed (a condition easily secured in making experiments with thermometer-bulbs), this

* To make the formula accurate, we should write $\int \frac{d\theta}{\theta}$ taken between the limits θ_1 and $\theta_1 - \Delta\theta_1$, instead of $\frac{\Delta\theta_1}{\theta_1}$, which is approximately its value when $\Delta\theta_1$ is small compared with θ_1.

becomes simply $A\frac{dQ}{dt}$, or

$$AV\sigma\rho_1\frac{\Delta\theta_1}{\theta_1}, \quad \ldots\ldots\ldots \quad (\epsilon)$$

where A is the area of the surface of the cooling body.

7. It will be instructive to compare the loss of heat by penetration with the quantity which is carried off by convection. To estimate the latter, let Ω be the section of the convection current, ρ its average density, $\Delta\theta$ the average excess of its temperature, and v its velocity. Then the total quantity of heat which will be removed per second by convection will be

$$\Omega v\sigma\rho\frac{\Delta\theta}{\theta}. \quad \ldots\ldots\ldots \quad (\zeta)$$

This is to be compared with (ϵ), the expression for the total loss of heat per second by penetration.

Now, in the cases that occur in laboratory experiments, $A\sigma\rho_1$ is seldom many times larger or many times smaller than $\Omega\sigma\rho$, but V is always very much larger than v, whence (ϵ) may have a value comparable with (ζ) while $\Delta\theta_1$ is very much less than $\Delta\theta$—in other words, when the processions between the opposed surfaces have but slightly different velocities. We learn from this that the escape by penetration may be expected to manifest itself as soon as the Crookes's layer has become in a moderate degree compressed *. It is also evident that the coexistence of a convection current will not much affect the escape of heat by penetration, inasmuch as convection currents are sluggish when compared with the promptness with which readjustments are made in Crookes's layers. It is therefore worth while to examine the numerous records of experiments upon the velocity with which bodies cool in gases, with a view to finding whether instances of the escape of heat by penetration can be found among them.

Part II. *Interpretation of Experiments.*

8. Accordingly I made a search of this kind last year, shortly after the publication of my two papers in the 'Philosophical Magazine,' but without finding any records more to the purpose than those by Dulong and Petit of experiments with hydrogen, which will be cited below; and as these, taken by themselves, did not seem sufficiently decisive, I postponed publishing further on the subject until I should have leisure to make experiments myself. But before this leisure came, Mr. George F. Fitzgerald met with a brief notice in Jamin's *Physique*, of experiments by De la Provostaye and Desains, which appeared to him to contain observations on the pene-

* Hence also thermal experiments may be expected to explore Crookes's layers with more sensitiveness than contrivances for manifesting the mechanical force which is also present.

tration of heat; and on referring to the original memoirs, first published more than thirty years ago in the *Comptes Rendus*, and afterwards with somewhat more detail in the *Annales de Chimie**, I had the pleasure of finding the record of two elaborate experimental investigations into what we now know to have been the penetration of heat. At that time the experimental results were regarded as anomalous; and the only conjecture which De la Provostaye and Desains put forward is that they may in some way depend on the swiftness of convection currents in attenuated gases †. It is, however, easy to see that no such increased swiftness as can exist will account for the observed phenomena. Mr. Fitzgerald was unable to spare the time necessary to follow up the subject, or he would have joined me in working out this part of the present memoir; but to him is due the whole credit of having perceived the importance of these observations, and to his kindness I owe the advantage of having had my attention directed to them and the permission to make use of them, as I now do.

9. Dulong and Petit, experimenting with large thermometer-bulbs placed at the centre of a hollow copper globe 30 centims. in diameter, blackened on the inside and kept at a constant temperature, observed the rate at which the thermometer, after having been warmed, cooled in different gases, at different tensions, and with the bulb naked or coated in various ways. From these experiments they obtained their well-known empirical law for the escape of heat by radiation and convection. The expression which they give consists of two terms; of which one represents the velocity with which heat escapes by radiation, and the other the velocity with which it escapes by convection, or, as we shall presently see, in some cases by convection and penetration. We have here no concern with the first of these two terms, further than to observe that the escape by radiation is the same at all tensions of the gas and for all dimensions of the receiver, and depends only on the character of the surfaces exposed, on θ_2 the temperature of the copper globe, and on $\theta_1 - \theta_2$ the excess of temperature of the thermometer. For given values of θ_1 and θ_2 it was accordingly a constant at all the tensions and with all the receivers

* *Comptes Rendus*, vol. xx. (1845) p. 1767, and vol. xxii. (1846) p. 77; *Annales de Chimie*, third series, vol. xvi. p. 381, and vol. xxii. p. 362.

† De la Provostaye and Desains conclude their second memoir in the following words:—"Nous ne chercherons à donner une explication complète des différents faits cités dans cette communication. Nous ferons remarquer seulement que le pouvoir refroidissant d'un gaz dépend de sa densité et de sa mobilité. Ces deux éléments varient en sens inverse quand on change la pression, et l'on conçoit que les effets de ces variations contraires puissent tantôt s'équilibrer, tantôt se surpasser dans un sens ou dans l'autre."

which De la Provostaye and Desains used, and in the following diagrams is represented by the interval between two horizontal lines. This interval is, moreover, small, because De la Provostaye and Desains reduced the loss by radiation to a very small amount by silvering or gilding the bulb of their thermometer.

The other term of Dulong and Petit's expression, which furnishes the rate of escape by convection, is

$$Kp^c;$$

where p is the tension measured in millimetres of mercury, K depends on the gas and on θ_1 and θ_2, and c was found to be nearly $\frac{1}{3}$ when the receiver contained hydrogen, but was nearly $\frac{1}{2}$ for the other gases experimented on and for atmospheric air. I will return to the case of hydrogen; but in the other gases the velocity of the escape of heat by convection with given temperatures of the bulb and receiver will be represented at different tensions of the gas by the ordinates of a curve not differing much from a parabola, since this would be the curve if the index were exactly $\frac{1}{2}$; and, accordingly, curves of this kind are laid down in the annexed diagrams. It is not material whether a large or a small portion of the parabola is introduced, because all parabolas are similar.

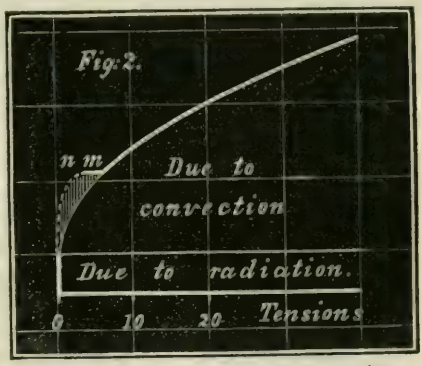
10. By thus plotting down the results of the experiments upon diagrams, we obtain the means of seeing at a glance how much of the escape of heat observed by De la Provostaye and Desains can be accounted for by radiation and convection, and how much remains to be allotted to penetration. De la Provostaye and Desains made their observations in three receivers—a hollow sphere of 24 centims. diameter, a hollow sphere of 15 centims. diameter, and a cylinder 6 centims. in diameter and 20 centims. in height; and they used in all the receivers the same thermometer, which had a cylindrical bulb 7 centims. long and 2 centims. across*. Accordingly the interval between the bulb and the walls of the receiver ranged from $8\frac{1}{2}$ centims. up to 11 centims. in the largest receiver, from 4 centims. up to $6\frac{1}{2}$ centims. in that of intermediate size, and was 2 centims. in the cylinder.

In Dulong and Petit's experiments the diameter of the receiver was 30 centims., and they used thermometers with spherical bulbs 2 and 6 centims. in diameter, so that the interval was either 12 or 14 centims.

11. With atmospheric air in the largest receiver (in which

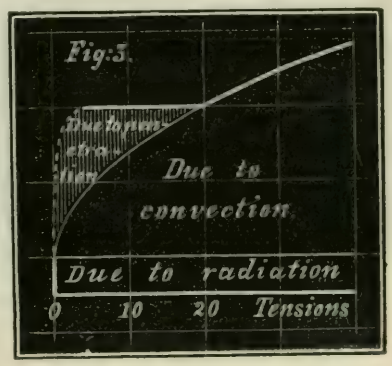
* The direction in which the heat penetrates, and of the Crookes's stress, will be perpendicular to the isothermal surfaces within the gas in the simple case which we have hitherto considered, where A is parallel to B; but it will in general pierce the isothermal surfaces obliquely if one part of the Crookes's layer is more curtailed than another.

a Crookes's layer of a width of $8\frac{1}{2}$ centims. would reach the walls at two points, and any wider Crookes's layer would be curtailed), De la Provostaye and Desains found that the rate of cooling, or the escape of heat per second, which is proportional to it, was represented by Dulong and Petit's expression (which had been based on experiments made with intervals of 12 and 14 centims.) until the exhaustion reached 6 millims. of mercury, but that, after passing that tension, the rate of cooling, instead of continuing to decrease, remained sensibly constant between tensions of 6 millims. of mercury and 2·8 millims. (the lowest tension at which they experimented). This is represented on fig. 2 by the horizontal line from *m* to *n*. In this figure the abscissas represent tensions in millims. of mercury, and the ordinates of the thick line represent the observed rates of cooling at different tensions but with constant values of θ_1 and θ_2. The part of the ordinate between the horizontal lines represents the escape by radiation; its continuation up to the parabola represents the escape by convection; and the extension upwards into the shaded portion of the figure is due to the penetration of heat across the Crookes's layer, which evidently reached the walls of the receiver when the tension was reduced to about 6 millims., and was compressed when the exhaustion proceeded further.



The shaded part is to be attributed to penetration.

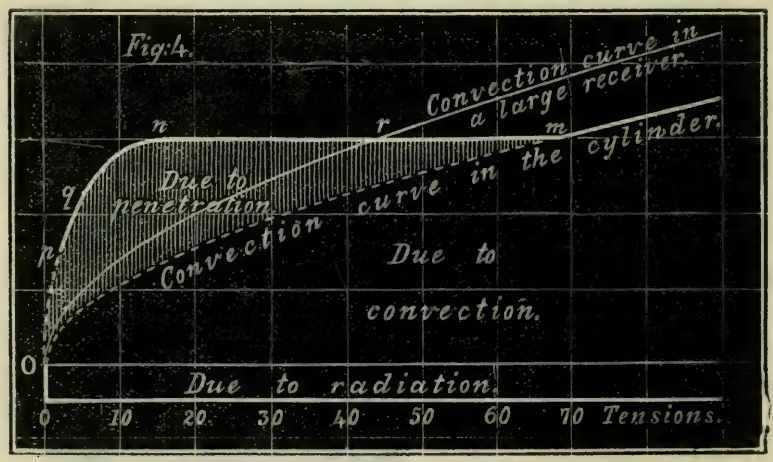
Similarly with the receiver of intermediate size, in which a Crookes's layer of a width of 4 centims. would reach the walls, the results obtained by De la Provostaye and Desains are represented graphically by fig. 3. In this case heat leaked away by penetration in appreciable quantities at tensions under 20 millims. of mercury, and kept the total



escape of heat nearly constant between tensions of 20 and 4 millims.

12. But the most decisive experiments were made with the cylindrical vessel, which was the smallest of the three receivers. In it the interval between the bulb and the walls of the vessel was only 2 centims.

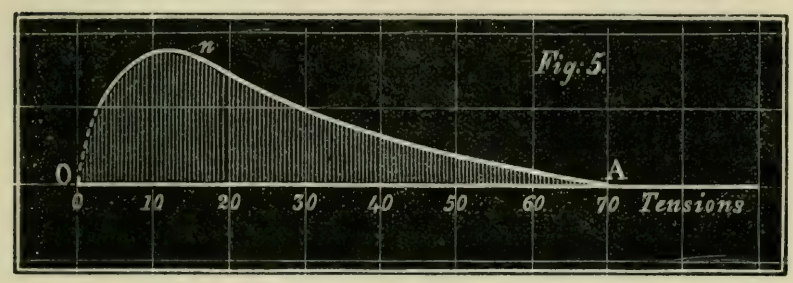
With this vessel the rate of cooling was *slower* than in the two larger receivers at all tensions from 760 millims., or the tension of an atmosphere, down to about 45 millims. This seems to indicate that the convection currents were impeded by the form and small size of the cylinder; so that if the ordinates of the parabola O r represent the rate of cooling which would result from convection in a large vessel, the ordinates of some lower curve such as O m will represent the rate due to convection in the cylinder. The observations recorded by De la Provostaye and Desains enable us to fix the points m, r, and n, corresponding to the tensions 70, 45, and 15 millims., nearly in a horizontal line. They also state that near the tension of 6 millims. the rate of cooling diminished with "excessive rapidity," but that nevertheless at a tension of 2·8 millims. it still exceeded by a large amount that which presented itself at the same tension in their largest receiver, and which is represented in fig. 2. These statements indicate that the observations, if plotted down, would have given a curve like the thick line of fig. 4. It is hardly necessary to point out that



the larger development of the phenomenon, and its exhibiting itself at higher tensions with each diminution of the size of the receiver, as shown in the foregoing diagrams, are in the

most satisfactory accordance with the theory presented in this memoir.

13. If we suppose the shaded portions of the ordinates in fig. 3 to be moved vertically downwards till they abut upon a horizontal axis of abscissas, we shall obtain the curve in fig. 5,

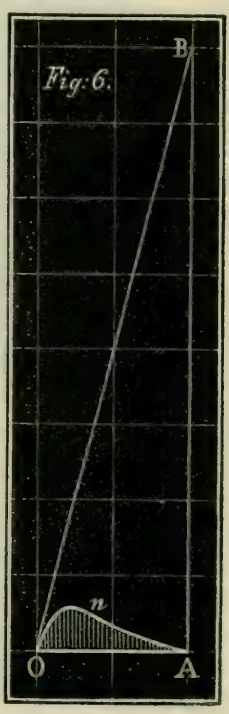


the ordinates of which represent the rate at which heat escaped by penetration in De la Provostaye and Desains's cylinder, separated from the effects of radiation and convection.

We can only compare this figure in a very general way with the formula given above for the escape of heat by penetration, viz.

$$\frac{dQ}{dt} = V\sigma\rho_1 \frac{\Delta\theta_1}{\theta_1}, \quad . \quad . \quad (\delta)$$

because too little is known of V, ρ_1, and $\Delta\theta_1$ to enable us to plot down a curve from this expression*. But we can, at all events, see that V will be only moderately affected by alterations of tension, that ρ_1 will vary nearly as the tension, and that as the tension is diminished $\Delta\theta_1$ will gradually rise from 0 to a value which is nearly $\frac{1}{2}(\theta_1 - \theta_2)$. Hence the curve must be one somewhat like that of fig. 6†, whose ordinates first rise gradu-



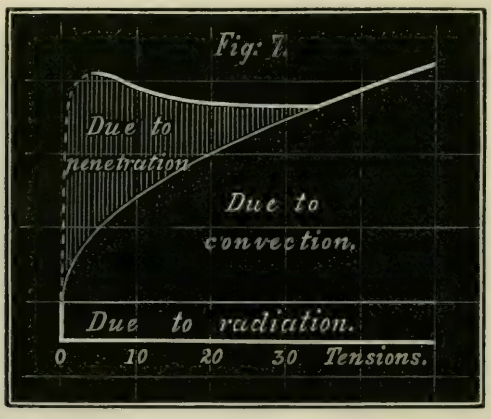
* Just as the parabolic curve of convection could not have been plotted down from equation (ζ), § 7, owing to the vagueness of some of the quantities which appear in it, viz. Ω, v, and $\Delta\theta$.

† In fig. 6, O B is intended to represent a portion of the curve $y = V\sigma\rho_1 \frac{1}{2} \frac{\theta_1 - \theta_2}{\theta}$, and O n A the result of shortening its ordinates in the ratio $\frac{\Delta\theta_1}{\frac{1}{2}(\theta_1 - \theta_2)}$.

ally to a maximum at a certain tension, after which they fall away to cipher if the exhaustion is continued indefinitely. This description agrees with the form determined from the observations and which is plotted down in fig. 5 ; so that the comparison, though necessarily very imperfect, lends support, so far as it goes, to the conclusion that the apparently anomalous escape of heat which De la Provostaye and Desains investigated was due to penetration.

14. Hitherto I have used only the observations recorded in the memoir first published in the *Comptes Rendus* for 1845. In their second memoir, first published in the *Comptes Rendus* for 1846, De la Provostaye and Desains record observations made with the silvered thermometer within their blackened cylinder, charged successively with hydrogen, carbonic anhydride, protoxide of nitrogen, and a mixture of air and hydrogen.

In carbonic anhydride the results of experiments are represented by fig. 7*. In this gas the total rate of cooling in-



creased when the tension was diminished from 12 to 4 millims. This observation took De la Provostaye and Desains so much

* De la Provostaye and Desains record the following observations, from which the curve in the text has been plotted down, the ordinates being drawn proportional to the reciprocals of the observed times of cooling:—

Tensions....	35 millims.	12 millims.	4 millims.
Times.....	m s 19 42	m s 19 38	m s 17 59

The reciprocals are proportional to 282, 283, and 309.

by surprise that they repeated and varied their experiments, till they were fully satisfied that the existence of the increased escape of heat was proved.

With protoxide of nitrogen (N_2O), a gas which has the same specific gravity as carbonic anhydride, their observations gave similar results. Between tensions of 35 millims. and 12 millims. the total rate of cooling remained nearly constant; and, as in carbonic anhydride, it was slightly increased by further diminishing the tension from 12 down to 4 millims. This slight increase was less in the protoxide of nitrogen than in the carbonic anhydride—about $\frac{1}{24}$ of the whole amount in the former gas, about $\frac{1}{12}$ in the latter.

The observations with these gases show that the form of the curve represented in fig. 5 is in an appreciable degree different in different gases, and that there are some gases in which the increase of the escape of heat by penetration when the tension is decreased will, within certain limits of temperature, exceed the decrease of the escape of heat by convection.

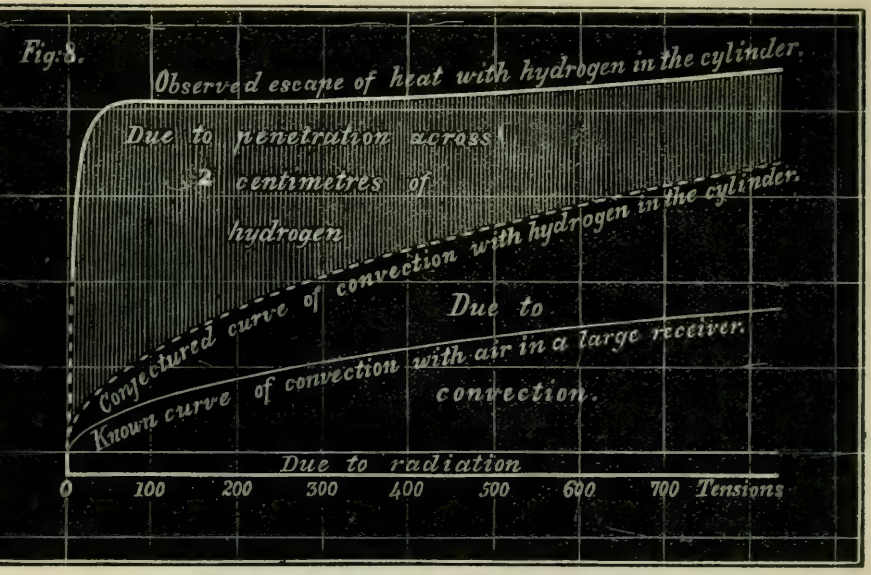
15. We now come to the very remarkable results which were obtained with hydrogen. They are plotted down in fig. 8. A Table of some of the results of the observations, and the following particulars recorded by De la Provostaye and Desains enable us to construct this figure. The loss of heat by radiation from the silvered bulb was only $\frac{1}{18}$ of the whole amount (presumably at 760 millims. tension). The rate of cooling at 20 millims. tension was found to be $\frac{11}{12}$ of that at 760 millims. The rate of cooling at a tension of 12 millims. was rather more than $\frac{11}{12}$ of that at 20 millims. At 4 millims. it fell to about one half; and nevertheless, when the rate of cooling at this lowest tension was compared with that of a similar bulb placed in the open air, it was found to exceed the latter in the proportion of 4 to 3. We thus get from the observations* all parts of the figure except those entered in dotted lines. The curve representing the loss by convection must lie

* The following observations are recorded by De la Provostaye and Desains:—

Tensions	760 millims.	477 millims.	57 millims.	20 millims.	4·4 millims.
Times of cooling..	m s 12 46	m s 13 20	m s 13 40	m s 14 49	m s 27 24

The rates of cooling will be as the reciprocals of these times, *i. e.* as the numbers 652, 625, 610, 562, and 304 respectively; and to these numbers the corresponding ordinates of the upper line in our figure have been made proportional.

everywhere below the upper line of the figure, and probably lies considerably above the curve representing the loss by con-

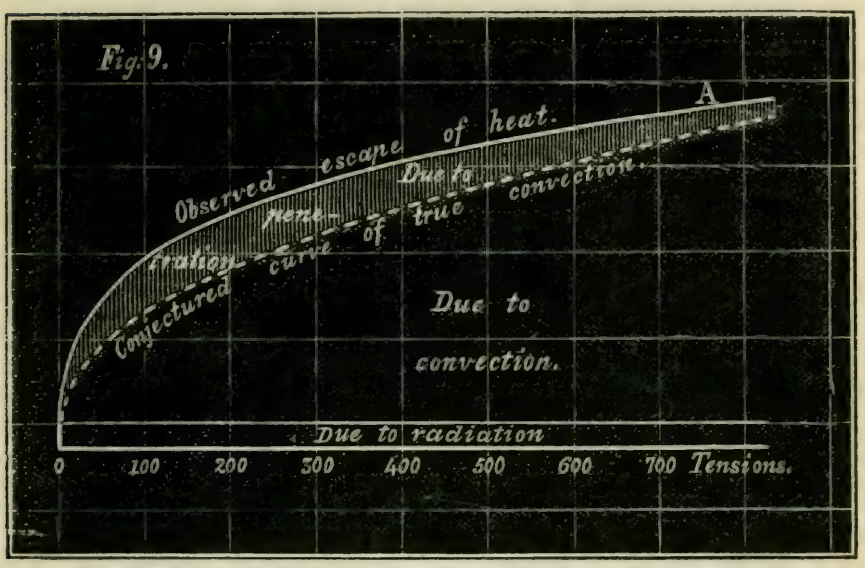


vection in air ; it therefore occupies some such position as the dotted line of the figure. The shaded interval between this dotted line and the upper line of the figure represents the enormous escape of heat to be attributed to the penetration of heat across two centimetres of hydrogen.

16. The observations previously made by Dulong and Petit on the rate of cooling in hydrogen come here to our aid. The interval between the walls of their receiver and the bulb was 12 or 14 centims.; and they found that, after allowing for radiation, the rest of the escape of heat within this receiver charged with hydrogen was proportional to $p^{0\cdot38}$; whereas in the other gases examined it was proportional to p in a power which differed slightly from one gas to another, but was in none far from $\frac{1}{2}$. The escape of heat with which they were here dealing, Dulong and Petit supposed to be wholly due to convection ; but we have now reason to suppose that, when the gas was hydrogen, penetration contributed largely to it, and was the reason why the index of p in Dulong and Petit's empirical formula was so different with hydrogen from its value with other gases. Accordingly, if we plot down the curve

$$y = kp^{0\cdot38},$$

in the upper line of fig. 9, to represent the observed excess of the escape of heat over what was accounted for by radiation



we may draw the dotted parabola crossing it somewhere to the right of A, and conclude that the convection, if it could be separated from penetration, would be represented by the ordinates of such a curve, and that the shaded interval between the two curves is due to heat having leaked away by penetration, across even so much as 12 centims. of hydrogen. Although we cannot assign the exact position of the dotted line until observations shall have been made in larger receivers, we can already see the general shape of the shaded space which is at present the object of our search.

17. In a mixture of air and hydrogen within the cylinder, De la Provostaye and Desains found that at a tension of 60 millims. the rate of cooling was "*much* less" than if the hydrogen alone had been present. From this, and from the observations plotted down in fig. 8, it follows that the Crookes's layer in such a mixture is narrower than if all the molecules present had been hydrogen. This accords with the theoretical consideration that the members of both the processions in the hydrogen will be more diverted from their course, and will therefore transmit forward less of their own momentum and *vis viva*, if some of the molecules they encounter are the heavier molecules of other gases.

18. Several phenomena observed by Grove, Tyndall, Mag-

nus, and others, have been attributed to copious conduction of heat through hydrogen. May we not with more probability refer them to the very remarkable power which hydrogen possesses of allowing heat to leak away by penetration? From the dynamical theory of gases, it seems improbable that any gas can possess true conducting-power in a high degree; and every observer must have been struck by the violence of the first chilling effect in some of these experiments, and the unflagging energy with which it is maintained, a promptness and persistence characteristic of penetration, but quite unlike the moderate initial effect and diminished subsequent progress which we should expect from conduction.

19. One of the most striking of these experiments is that by Sir William Grove, which exhibits the cooling effect of hydrogen on a wire rendered incandescent by the passage of an electric current; and according to the hypothesis here presented it ought to be possible to repeat this experiment *in ordinary atmospheric air* by bringing the incandescent wire sufficiently close to a cool object. This very instructive experiment was proposed by my son, Master Gerald Stoney, and has been successfully performed by him. He first passed the wire through a glass tube drawn out sufficiently thin. The effect could then be seen; but it was evanescent, because the glass became rapidly heated. No doubt, if the tube had been surrounded by a water jacket, the experiment might have been made in this way satisfactorily. But he made it in an equally permanent form, and with greater ease, by simply bringing the incandescent wire close to a tin can containing water, to which the heat leaked away abundantly from the wire when the intervening stratum of air was sufficiently thin. The effect is best seen when the wire is of a dull red, on account of the ease with which the eye detects the difference between dull red and darkness. It then becomes conspicuous when the interval is a millimetre, and can be perceived when the interval is considerably more. In this experiment the can was at a slightly higher temperature than the room. On this account, and because a small part of the radiated heat was reflected back on the wire by the tin, the loss of heat by radiation was less than when the can was away; moreover the convection current was enfeebled by being both cooled and obstructed by the neighbouring obstacle. Hence the true loss of heat by penetration must have been in excess of that which manifested itself.

20. Another phenomenon which admits of explanation by the theory developed here and in my former papers, is one which is said to have caused the bursting of steam-boilers,

which is familiar to us as the way in which a laundress tests the heat of her smoothing-iron, and which was studied by M. Boutigny under the name of the spheroidal state of liquids. If a drop of water or other cold volatile liquid is allowed to fall into a smooth and sufficiently hot metal dish, it continues liquid instead of flashing off into vapour, and exhibits an appearance of great mobility. Here the liquid settles down upon the Crookes's layer which envelops the metal, and reduces that portion which is under it to the condition of a compressed Crookes's layer. Now the mechanical peculiarity of a compressed Crookes's layer is, that it exerts more force in the direction along which the heat travels (in the present instance up and down) than in the perpendicular direction; and inasmuch as the pressure sideways *must* continue to be the pressure of the atmosphere, the excess of pressure upwards is able to support a weight. When we also remember that this excess of pressure would be augmented by still further curtailing the Crookes's layer, *i. e.* by depressing any part of the drop, we have all the mechanical conditions necessary for the *stable* equilibrium of the drop, if only the force rises to a sufficient amount before the drop settles down quite through the Crookes's layer. This, by the theory, depends altogether on the difference of temperatures which can be maintained. The first thermal effect is, that the drop becomes warmed by the radiation and penetration of heat from the hot metal below. This causes the liquid, if volatile, to lose heat by evaporation, and, in most cases, to lose a little heat also by radiation to surrounding bodies. As the temperature of the drop rises, the heat thus lost increases, while at the same time the heat received from below diminishes, and if a balance between the two is effected before the liquid reaches the boiling-point, the drop continues liquid, the temperature remains henceforth unchanged, and we have before us the striking spectacle of a liquid in the spheroidal state.

21. I have long thought it likely that the drops which may be sometimes seen running over the surface of a volatile liquid are supported by compressed Crookes's layers intervening between them and the liquid on which they float—that they are, in fact, drops in the spheroidal state; and the following observations abundantly confirm this suspicion. These floating globules are easily formed when a liquid as volatile as spirits of wine is allowed to fall in drops of a medium size from a height of about 8 centimetres into a vessel containing some of the same liquid moderately warmed*. They can also be

* A better way to form them is gently to lay the drop as it were with a fine pipette upon the surface of the heated liquid. The drop when

occasionally produced by dropping the spirits of wine upon water. And every one is familiar with them when, in some states of the weather, they roll about in numbers on allowing water to drip from an oar upon the sea. Recently they were abundantly produced by splashing the water of a neighbouring pond; and I took advantage of the opportunity to ascertain that the conditions required by the hypothesis were fulfilled. The temperature of the air was about 15°, that of the surface of the water 18¼°; and a very dry breeze was blowing, which so facilitated evaporation from the drops* that they probably maintained a temperature as low as 10°, a temperature which my thermometer reached when I left a damp weed in contact with one side of the bulb.

When globules of methylated spirit were formed upon a beaker nearly full of the same liquid, which was progressively warmed, it was found that, when the air was still, there was a particular temperature at which the drops were most persistent. At this temperature some lasted for as long as twelve or fourteen seconds. As the temperature rose beyond this point, the atmosphere of vapour impeded evaporation and the persistence of the drops became less; but by gently blowing on the surface so as to accelerate the evaporation, it was found possible to keep some of the smaller drops in existence for two or three minutes †, during which time they very slowly dwindled away till they were very minute, and then suddenly vanished. When the temperature of the beaker full of spirit was allowed to fall below the point above referred to, the duration of the drops also became progressively less; but they could still be formed, though short-lived, at a temperature a little below that of the room.

From this, and from the circumstance that I succeeded in forming some within a bottle of methylated spirit which had been standing open for a while, and within which evaporation must have been feeble, it is evident that a drop can be sup-

formed can be fed from the pipette and so greatly augmented in size. When in this way the drop is made so large as to be very much flattened out, tremulous motions arise similar to those which Boutigny observed in his spheroidal drop, but less violent.

* The liquid on which the drops rest is no doubt also cooled by evaporation, but in a trifling degree, because convection currents constantly bring to the surface an accession of warm liquid from below.

† In four better-arranged experiments, since made in the laboratory of the Royal Dublin Society by Mr. R. J. Moss and myself, and of which we hope to give an account to the Society, we succeeded in maintaining similar drops of larger size formed on methylated ether for ten, fourteen, sixteen, and twenty-six minutes, respectively; and we believe that it will not be difficult, by securing a greater constancy in the conditions indicated by the theory, to prolong their existence very much more.

ported with but a slight difference of temperature between it and the liquid on which it rests. In this respect the spheroidal state on liquids differs from that in which the drop rests upon a heated solid. The difference of behaviour is probably due to the deformation of its natural spherical shape to which a drop is compelled to submit when it rests on a rigid surface. Owing to this constraint the surface-tension over the drop will force some parts into closer contact; and, moreover, the vibrations which always arise in this case must tend to a similar result. On the other hand, when the drop is resting on a liquid, it settles tranquilly into a beautiful concave socket that can be seen by looking at the surface of the fluid from beneath. This socket allows the globule to retain a nearly spherical and therefore unconstrained form; and, accordingly, the opposed surfaces come within an approximately equal distance of one another throughout a large arc. And it is evident that as the whole pressure arising from the molecular motions in the air would support a column of spirits of wine $11\frac{1}{2}$ metres high, it needs only a very moderate Crookes's polarization of the stratum of air to furnish that slight preponderance of momentum in a determinate direction which is required to support the few additional millimetres that correspond to the weight of the drop. We must remember, too, that a drop may, under favourable circumstances, outlive the difference of temperature, because it would take a sensible time for so slight a pressure as the weight of the drop to squeeze the film of air, when once established, out of its narrow chink. Even a heavy metal proof-plane will float over another proof-plane, upon the stratum of air entangled between them, for a considerable time.

22. Professor Barrett has called my attention to another unexplained phenomenon, of which we can now see the cause, viz. the mobility imparted to a very fine powder (as, for example, magnesium carbonate or precipitated silica) by heating it in a metal dish. When the dish is disturbed the powder glides about as if floating; and it is in fact floating on the compressed Crookes's layer, which will spring into existence whenever the powder is able by radiation to maintain a lower temperature than the dish.

23. The communication of heat by penetration is a very familiar phenomenon; for when surfaces at different temperatures are brought into what is commonly called contact, there is usually a thin intervening stratum of air, except at special points; and, accordingly, the greater part of the transfer of heat, so long as the difference of temperature is considerable, must be effected, not by contact, but by penetration across a Crookes's layer.

LVII. *The Spectra of Chemical Compounds.* By James Moser *.

IS spectral analysis indeed entitled to be ranked as a branch of qualitative analysis?

Is the spectrum of a compound the sum of the spectra of the component elements?

From an observation of the spectrum of a compound, is it possible to determine the nature of the elements in the compound, or has each compound a characteristic spectrum of its own?

The discoverers of spectral analysis, Kirchhoff and Bunsen, in their first memoir, said that "differences in the compounds of any given metals have no influence upon the position of the lines indicative of the presence of the individual metals." This opinion has been generally accepted as true. The possibility of each compound possessing a characteristic spectrum was, however, recognized by Kirchhoff and Bunsen. Elsewhere they say, "It is possible that the salts which we volatilized suffered decomposition at the temperature to which they were raised in the flame, and that the lines which we observed were really due to the presence of *free metals*; it is possible also that each chemical compound may show lines other than those caused by the elements composing it"†.

The object of the present paper is to show that each chemical compound really possesses a characteristic spectrum of its own. A chemical compound is characterized by "the difference between its properties and the properties of its component elements . . .; the properties of the elements are lost in those of the compound; the individuality of the elements has disappeared in the formation of a new body with new properties"‡.

Those physicists who have studied the subject now under consideration have generally made observations on emission-spectra only.

This method is open to serious objection, and must be superseded, if trustworthy results are to be obtained, by the study of absorption-spectra.

In studying the literature connected with the spectra of chemical compounds, it is interesting to observe how the original view of Kirchhoff and Bunsen is gradually abandoned. A. Mitscherlich found that the metallic oxides and chlorides, when brought into the flame, afforded spectra different from

* Translated and condensed from Pogg *Ann.* clx. pp. 177–199, by M. M. Pattison Muir, The Owens College, Manchester.

† Pogg. *Ann.* cxiii. 381.

‡ Hofmann, *Einleitung in d. mod. Chemie*, Cap. iii.

those obtained by bringing the metals themselves into the electric arc. His observations have been confirmed and extended by Diacon, by Lecoq de Boisbaudran, and by Lockyer.

Plücker and Hittorf obtained different spectra from such non-metals as nitrogen, sulphur, selenium, and carbon, by varying the conditions under which the spectra were produced. Nitrogen, for instance, showed two band-spectra, and one line-spectrum; compounds of carbon with oxygen, nitrogen, and hydrogen yielded five different spectra, which were all regarded as spectra of the element carbon, the differences being attributable to the influence of temperature. Ångström and Thalén regarded the different spectra obtained by Plücker and Hittorf as caused by the different carbon compounds examined by them: the line-spectrum of nitrogen they looked on as the spectrum of the element itself; one of the band-spectra they regarded as that of nitric oxide; the second band-spectrum they could not explain*.

Kirchhoff obtained different spectra from calcium chloride by varying the conditions under which the salt was volatilized. The spectrum produced by using an electric current of very weak intensity was the same as that noticed when the salt was brought into the gas-flame. By employing a current of greater intensity, or a flame of gas and air, a different spectrum was produced. Mitscherlich's experiments, in which he obtained the spectrum of calcium oxide by bringing a mixture of calcium and ammonium nitrates into a flame of gas and air, and the spectrum of calcium chloride by volatilizing the chloride in a flame of hydrogen and chlorine, seemed to point to an explanation of the phenomena noticed by Kirchhoff. The spectrum obtained when a current of low intensity was employed was probably due to undecomposed calcium chloride, mixed, especially towards the close of the experiment, with calcium oxide; when a stronger current was employed, the chloride and oxide were probably dissociated, and lines due to the presence of the elements began to appear: this dissociation was rendered complete by using a current of great intensity; the lines which then appeared were entirely caused by the elements in the free state.

But the study of emission-spectra alone cannot enable us to answer the question, Has each chemical compound a distinct spectrum of its own? Emission-spectra tell us that the ele-

* Helmholtz supposes that the chemical atoms yield line-spectra, the molecules (or complexes of atoms) band-spectra. In accordance with this view, Plücker's nitrogen-spectrum of the second order would be caused by nitrogen atoms, and that of the first order, which was not explained by Ångström and Thalén, by nitrogen molecules.

ment whose lines we observe is at one time chemically combined, and at another in the free state; but these spectra do not allow us to associate the presence of a distinct compound with a definite temperature. If the temperatures at which observations are made be varied, Kirchhoff's fundamental proposition forbids us to suppose that the spectra should remain unaltered.

But the observation of absorption-spectra enables us, I believe, to answer the question already proposed, and to answer it in the affirmative.

My experiments show that large alterations in the mass of material and in the temperature are without material influence upon the absorption-spectra examined by me; hence the differences noticed in these spectra cannot be attributed to either of those causes.

The question arises, whether absorption-spectra alone, without the simultaneous observation of emission-spectra, are sufficient to characterize chemical substances. This question may, I think, be answered in the affirmative. The molecules of some substance, iodine for instance, may be regarded as vibrating so as to give forth light; and at the same time they may absorb a portion of the white light passing through them; if the temperature be decreased a point will be reached at which the vibrations will not be sufficiently rapid to produce light, but the molecules will nevertheless continue to absorb light. But it cannot be supposed that at this point Kirchhoff's fundamental proposition should cease to hold good.

The following experiments show an analogy between absorption- and emission-spectra: the former behave themselves at low temperatures analogously with the latter at high temperatures; changes in the intensity of the absorption-bands are observable coincident with changes in mass and in temperature.

The experiments were carried out with iodine, with bromine, and with nitrogen tetroxide. I shall first describe those experiments in which mass of material underwent variation.

The apparatus was arranged so that two spectra could be simultaneously brought into the field of vision. Thalén's absorption-spectrum of iodine served as a scale with which to compare the bromine-spectrum. The following numbers express the wave-lengths of the bromine absorption-lines. I have numbered the lines, beginning with that corresponding with D, +1, +2, &c. in the blue, and −1, −2, &c. in the red:—

		Difference.			Difference.			Difference.
−15	625·6	1·4	−3	594·1	2·7	+10	555·5	2·7
−14	624·2	6·4	−2	591·4	0·6	11	552·8	2·4
−13	617·8	1·5	−1	590·8	3·3	12	550·4	2·8
−12	616·3	4·6	+1	587·5	4·0	13	547·6	2·4
−11	611·7	1·7	+2	583·5	3·4	14	545·2	2·2
−10	610·0	3·2	3	580·1	3·7	15	543·0	2·0
− 9	606·8	1·7	4	576·5	3·5	16	541·0	1·6
− 8	605·1	2·5	5	573·0	3·9	17	539·4	3·6
− 7	602·6	2·4	6	569·1	3·3	18	535·8	2·0
− 6	600·2	1·4	7	565·8	3·6	19	533·8	4·6
− 5	598·8	3·4	8	562·2	3·4	20	532·2	3·0
− 4	595·4	1·3	9	558·8	3·3	21	529·2	1·4
− 3	594·1		10	555·5		22	527·8	

In order that the whole of these lines should be observed, it was necessary to vary the thickness of the absorbing layer. For this purpose the bromine vapour was contained in a wedge-shaped glass vessel; the light was allowed to pass through the thicker part when observations were made in the red, and through the thinner part when observations were made in the blue.

At a temperature of about 20°, the lines from −1 near D to +22 in the blue were recognizable with a bromine layer 10 millims. in thickness. By increasing the thickness of the layer the *whole of the lines* became more intense, and the lines −2, −3, to −14 in the red gradually appeared. The fine lines appearing as shading in the blue gradually became more apparent, extending towards the red until the space between any two lines became equally dark; continuous absorption thus spread slowly towards the red.

With a layer 10 millims. in thickness the spectrum between the lines −1 and +22 was observed.

With a layer 6 millims. in thickness the spectrum between the lines −6 and +12 was observed.

With a layer 8 millims. in thickness the spectrum between the lines −11 and +8 was observed.

Increasing the thickness of the layer thus produced an equal (intensifying) effect upon all portions of the spectrum, but did not cause changes in special parts of the spectrum. Increasing the thickness of the absorbing layer, then, only caused the spectrum to become more marked in its character.

Observations on the absorption-spectra of iodine and of nitrogen tetroxide confirmed those made with bromine.

Alteration of temperature produces different effects upon different parts of the spectrum.

A glass tube 80 millims. in length and 15 millims. in width was filled with bromine vapour; no liquid bromine was present at the ordinary temperature. The lines from −1 near D to +23 in the greenish-blue were observable. The tube was warmed by means of a Bunsen's lamp: the lines −2, −3, −4, to −6 became visible; the area of total absorption advanced from the blue end until it reached the line +12. The temperature of the bromine was determined by observing the melting of little pieces of various metals brought into the tube, to be about 350°. Increasing the temperature had thus caused the lines from −2 to −6 to become visible. I have already stated that increasing the thickness of the bromine layer also caused lines in the red to appear: I found by actual experiment that an increase in temperature from 20° to 350° was equal, in this respect, to increasing the thickness of the layer from 15 to 16 millims.

Analogous results were obtained with the spectra of iodine and of nitrogen tetroxide.

The following observations regarding effects of increased temperature relate to individual lines in each of the three spectra examined: these effects were not produced by increasing the thickness of the absorbing layer, but only by increasing the temperature. The two lines referred to diminished in intensity, and finally disappeared, when the temperature was increased, while the intensity of the neighbouring lines, as also that of the whole spectrum, was increased.

Bromine, iodine, and nitrogen tetroxide were warmed in sealed tubes 80 millims. in length and 15 millims. in width: the following lines disappeared:—

(1) In the bromine-spectrum.
  (*a*) The line +12; the space between 11 and 13 gradually became filled with fine lines.
  (*b*) The line +15; the space between 14 and 16 became filled with fine lines.

(2) In the iodine-spectrum.
  A line nearly in the same position as the bromine-line 15, the space between the two neighbouring lines becoming filled with fine lines.

(3) In the nitrogen tetroxide spectrum.
  Three lines close by C, standing out some distance from one another.

Weiss* says that he noticed a change in the position of certain lines in the absorption-spectrum of nitrogen tetroxide, produced by increasing the thickness of the layer of gas, or by raising the temperature. My own experiments have convinced me

* Pogg. *Ann.* cxii. p. 155.

that Weiss's observations are erroneous. If a poor apparatus be employed, the lines already mentioned in the spectrum of nitrogen tetroxide appear to grow thicker when the temperature is raised; the middle of the lines appears to occcupy a new position. But if the same experiment be made with a superior apparatus, it is found that a number of new fine lines have appeared, and that there has been no real alteration of the position of the original line.

Weiss's so-called "change in the position of the lines" is thus shown to be a phenomenon exactly similar to that which occurs when the D line is observed through a good spectroscope: instead of seeing one line, two become apparent.

These observations on absorption-spectra enable us to understand how valuable such spectra are in determining the chemical nature of any substance. Before, however, we can say that each and every chemical compound possesses a characteristic spectrum of its own, it would be necessary for us to observe a very large number of absorption-spectra. Much remains to be done in this direction. So far as experiment goes, we know of no facts which positively contradict the assertion that for each compound there is a characteristic absorption-spectrum. The same absorption-spectrum is said to be common to more than one oxide of chlorine; but we really know very little concerning the exact composition of these bodies. Although I have endeavoured to show that alteration in temperature and in mass of material produces but slight alteration in absorption-spectra, nevertheless I must not be looked on as denying the possibility of several spectra being possessed by one and the same element. The experiments of Plücker and Hittorf, of Lockyer, &c. show that certain elements do possess more than one spectrum. The spectra obtained at low temperatures may probably be regarded as caused by the molecules of the elements, while those obtained at high temperatures may be looked on as caused by the atoms.

A systematic observation of absorption-spectra, with especial reference to the course of chemical change in solutions, would certainly be of much assistance in solving some of the problems of physical chemistry.

LVIII. *A Theoretical Deduction of the best Resistance of a Telegraph Receiving-instrument.* *By* R. S. Brough*.

THE information given in the text-books regarding the proper resistance of an electromagnetic receiving-instrument to employ on any telegraphic circuit is meagre and indefinite. The authors usually content themselves with saying

* From the Proceedings of the Asiatic Society of Bengal for August 1877. Communicated by the Author.

that on short circuits the instruments should be wound with thick wire, while on long circuits they should be wound with fine wire.

Professor Fleeming Jenkin, in his 'Electricity and Magnetism,' however, states that the resistance of the receiving-instrument should not be more than a moderate fraction of the resistance of the whole circuit. In a footnote, he adds that some authority (unnamed) recommends that the resistance of the receiving-instrument should be $\frac{5}{16}$ of that of the whole circuit, and remarks that this appears to be a very large value.

Mr. Schwendler, in his 'Testing Instructions,' published under the authority of the Director-General of Telegraphs in India, taking into consideration the influence of want of perfect insulation of the line-wire, deduces that the resistance of the receiving-instrument should be $\frac{5}{8}$ of that of the line-wire.

The fact of the matter is, that on comparatively short lines and at low speeds of signalling (say twelve words per minute) the resistance of the receiving-instrument is not of much importance, as deficiency of sensibility can be compensated by increased battery-power, and the circuit will appear to work equally satisfactorily whether the resistance of the receiving-instrument be 500 or 2500 ohms.

In such cases the general rule given in the text-books is sufficient for practical purposes.

When we come, however, to the case of high-speed signalling*, or of very long and highly insulated lines, the question assumes a different phase, and becomes one of great importance.

Now the best resistance for an electromagnet to be employed as a receiving-instrument on any line has to be considered from two aspects, which may fitly be referred to as the "static" and the "kinetic."

Considered under the first aspect the problem is a purely statical one: it is to find the resistance of the receiving-instrument which will make its magnetic force a maximum when a steady current is flowing from the sending to the receiving station. By a steady current is meant one which does not vary in strength with respect to time. This problem is completely solved and thoroughly understood.

It can be shown† that the magnetic force is a maximum for

$$r=\sqrt{ki}\left\{\frac{\sqrt{ki}(1-\epsilon)^{-2l}\sqrt{\frac{k}{i}}+f(1+\epsilon)^{-2l}\sqrt{\frac{k}{i}}}{\sqrt{ki}(1+\epsilon)^{-2l}\sqrt{\frac{k}{i}}+f(1-\epsilon)^{-2l}\sqrt{\frac{k}{i}}}\right\},$$

* For high-speed telegraphy, electromagnetic receivers are being superseded by electro-chemical receivers, which are free from mechanical and magnetical inertia.

† Blavier, *Annales Télégraphiques*, 1858, p. 234.

where r = resistance of receiving-instrument,
f = „ battery,
k^* = conduction per unit of length,
i^* = insulation,
and l = length of line.

If the resistance f of the battery may be neglected,

$$r = \sqrt{ki}\,\frac{1-\epsilon^{-2l\sqrt{\frac{k}{i}}}}{1+\epsilon^{-2l\sqrt{\frac{k}{i}}}}$$

= measured resistance of line with its distant end to earth.

From this value of r a considerable reduction has to be made, on account of the thickness of the insulating covering of the wire in the receiving-instrument, according to the formula†

$$\frac{\text{resistance of receiving-instrument}}{\text{external resistance}} = \frac{\text{diameter of bare wire}}{\text{diameter of covered wire}}.$$

Considered under the second aspect, the problem is a kinetic one. Here the current is not assumed to be steady ; but the influence of the resistance of the receiving-instrument on the rapidity of the variation of the potential of the line is considered—that is to say, its influence on the speed of signalling, since signalling is simply causing the potential at the receiving end of the line to vary in some preconcerted manner. This problem has never been completely solved.

Sir William Thomson, however, has shown that when the resistance of the receiving-instrument is not very great as compared with the resistance of a perfectly insulated line, its effect is the same on the speed of signalling as if the line had been lengthened by a piece whose resistance would be equal to that of the receiving-instrument.

Sir William Thomson has further shown that the speed of signalling on any line depends on the value for that line of a

* Let
A = measured insulation of line, distant end insulated,
and
B = „ conduction „ „ to earth.
Then
$$k = \frac{\sqrt{AB}}{2l}\log_\epsilon \frac{\sqrt{A}+\sqrt{B}}{\sqrt{A}-\sqrt{B}},$$
and
$$i = \frac{AB}{k}.$$

† See Proceedings of the Asiatic Society of Bengal, June 1877.

certain constant, which may be called the "retardation characteristic" of the line, and the expression for which is

$$\mathrm{RC} = \frac{kcl^2}{\pi^2} \log_\epsilon \left(\tfrac{4}{3}\right);$$

where k is the resistance and c the capacity of the line per mile, and l is the length of the line in miles.

Now we see that the value of the RC increases as the square of the length of the line; and since by increasing the resistance of the receiving-instrument we virtually increase the length of the line, it is perfectly obvious that, if we make the resistance of the receiving-instrument unduly high, we may increase the value of the RC to such an extent as to impair the signalling-speed of the line.

It thus becomes clear that in the case of a very *long* and *highly insulated* line the best resistance for the receiving-instrument, as indicated by the result obtained by examining the problem under the first aspect only, may be so great as to retard the speed of signalling.

I shall here consider only the case of a perfectly insulated line.

Let l = the length of the line in miles,
k = resistance per mile in ohms (supposed uniform),
c = capacity per mile in farads (suposed uniform),
and r = the resistance in ohms of the receiving-instrument.

Then the sensibility of the receiving-instrument is

$$\mathrm{M} = \text{const.} \times \frac{\sqrt{r}}{r + kl}.$$

And assuming that the intercalation of the receiving-instrument of resistance r in circuit has approximately the same influence on the signalling-speed as increasing the length of the line by $\frac{r}{k}$ miles, we have

$$\mathrm{RC} = \text{const.} \times \frac{kc\left(l + \frac{r}{k}\right)^2}{\pi^2} \log_\epsilon \left(\tfrac{4}{3}\right).$$

Now, if it be assumed that the efficiency of the receiving-instrument varies directly as its sensibility, but inversely as its retardative influence, then we have the following expression for the efficiency, namely

$$\mathrm{RE} = \text{const.} \times \frac{\pi^2 \sqrt{r}}{kc\left(l + \frac{r}{k}\right)^2 (r + kl) \log_\epsilon \left(\tfrac{4}{3}\right)}$$

$$= \text{const.} \times \frac{\sqrt{r}}{(r + kl)^3},$$

which is a maximum for

$$r = \frac{kl}{5};$$

that is, the resistance of the receiving-instrument in the case of a perfectly insulated and uniform line should be one fifth of the resistance of the line*.

Taking into consideration the resistance of the signalling-battery, which has hitherto been neglected, the result is modified as follows.

Suppose we are given a certain number of cells (all of equal electromotive force and resistance) and arrange them so that the total resistance of the battery $= f$; then it may easily be shown that the total electromotive force of the battery will be proportional to $\sqrt{f}$.

Thus the expression for the sensibility of the receiving-instrument becomes (employing the same notation as before)

$$\mathrm{M} = \text{const.} \times \frac{\sqrt{fr}}{f + r + kl};$$

and the expression for the retardation characteristic becomes

$$\mathrm{RC} = \text{const.} \times \frac{kc\left(l + \frac{f+r}{k}\right)^2}{\pi^2} \log_e\left(\tfrac{4}{3}\right);$$

and, finally, the expression for the receiving-efficiency of the instrument becomes

$$\mathrm{RE} = \text{const.} \times \frac{\sqrt{fr}}{(f + r + kl)^3},$$

which has a maximum both with respect to f and to r, namely for

$$\left.\begin{aligned} r &= \tfrac{1}{5}(f + kl), \\ r &= \tfrac{1}{5}(r + kl). \end{aligned}\right\}$$

These maxima conditions are simultaneously fulfilled by

$$r = f = \tfrac{1}{4} kl.$$

* Singularly enough, this is the precise value selected, on experimental grounds, by Professor Hughes.

LXI. *On a General Theorem respecting Electrical Influence.* *By* Professor R. Clausius*.

CERTAIN reciprocity-theorems respecting the reciprocal influence of two conductors of electricity have already been repeatedly advanced by various authors. I take leave to communicate here a very general, and, so far as I know, new theorem, from which several of those theorems result as immediate consequences.

Given any number whatever of conducting bodies C_1, C_2, C_3, *&c., which act by way of influence on each other. These are to be charged with electricity in two different ways. In the first charge let the quantities of electricity present upon the individual bodies be*

$$Q_1, \quad Q_2, \quad Q_3, \text{ \&c.},$$

and the levels of potential thereby produced on the bodies

$$V_1, \quad V_2, \quad V_3, \text{ \&c.};$$

and in the second charge let the quantities of electricity and the potential-levels be

$$\mathfrak{Q}_1, \quad \mathfrak{Q}_2, \quad \mathfrak{Q}_3, \text{ \&c.},$$
$$\mathfrak{V}_1, \quad \mathfrak{V}_2, \quad \mathfrak{V}_3, \text{ \&c.}$$

Then the following equation holds good:—

$$V_1\mathfrak{Q}_1 + V_2\mathfrak{Q}_2 + V_3\mathfrak{Q}_3 + \text{\&c.} = \mathfrak{V}_1Q_1 + \mathfrak{V}_2Q_2 + \mathfrak{V}_3Q_3 + \text{\&c.} \quad \text{(I.)}$$

or, employing summation-symbols, more briefly written,

$$\Sigma V\mathfrak{Q} = \Sigma\mathfrak{V}Q. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(I a.)}$$

For the proof of this equation, let us imagine an infinitely large spherical surface formed round a point situated in the vicinity of the bodies, and to the infinite space lying between the bodies and the spherical surface apply the well-known equation of Green, while we denote the two functions therein occurring by V and $\mathfrak{V}$, understanding by these the potential-functions corresponding to the first and second charges respectively. The equation will then read:—

$$\int V\frac{\partial\mathfrak{V}}{\partial n}\,d\omega + \int V\Delta\mathfrak{V}\,d\tau = \int \mathfrak{V}\frac{\partial V}{\partial n}\,d\omega + \int \mathfrak{V}\Delta V\,d\tau. \quad . \quad \text{(1)}$$

Here $d\omega$ signifies an element of the surface which bounds the space we are considering, and which consists of the surfaces of the given bodies and the infinitely large surface of the sphere; n is to represent the normal erected upon the surface-element (reckoned positive in the direction of the space considered); and the integrals containing $d\omega$ refer to the total limiting surface. Futher, $d\tau$ denotes an element of the space

* Translated from a separate impression, communicated by the Author, from Poggendorff's *Annalen*, new series, vol. i. pp. 493–499.

considered, by Δ is signified the operation $\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}$, and the integrals which contain $d\tau$ are to be extended over the entire space under consideration.

But now, with both the adopted methods of charging, no electricity is contained in this space; and consequently there hold good in it everywhere the equations

$$\Delta V=0 \text{ and } \Delta \mathfrak{V}=0,$$

by which equation (1) reduces to

$$\int V\frac{\partial \mathfrak{V}}{\partial n}\,d\omega=\int \mathfrak{V}\frac{\partial V}{\partial n}\,d\omega. \quad . \quad . \quad , \quad . \quad (2)$$

In this equation also occurs a simplification. The two integrals are, according to the above, to be taken over the surfaces of the given bodies and over the spherical surface. But now, if R signifies the infinite radius of the spherical surface, the values of V and $\mathfrak{V}$ on that surface are infinitesimal quantities of the order $\frac{1}{R}$, and the values of the differential coefficients $\frac{\partial V}{\partial n}$ and $\frac{\mathfrak{V}}{\partial n}$ at which the direction of the normal coincides with that of the radius are infinitely small quantities of the order $\frac{1}{R^2}$. The products $V\frac{\partial \mathfrak{V}}{\partial n}$ and $\mathfrak{V}\frac{\partial V}{\partial n}$ are consequently, on the spherical surface, infinitesimal quantities of the order $\frac{1}{R^3}$. As for the surface-element of the spherical surface, we can replace it by the product $R^2 d\sigma$, if $d\sigma$ denotes an element of the solid angle at the centre of the spherical surface. Then the factor, on both sides of the equation, with which $d\sigma$ under the integral-symbol is affected is an infinitesimal one of the order $\frac{1}{R}$, whence it follows that, of both integrals, the part which refers to the spherical surface, and which is to be taken according to σ from 0 to 4π, is infinitely small and may be neglected. Consequently the integrals in equation (2) need only to be referred to the surfaces of the given bodies.

On the surface of each body the potential-function is constant; hence, for the part of the integral which refers to it, it can be taken out of the symbol of the integral. Accordingly we can write equation (2) thus:—

$$\left.\begin{aligned} &V_1\int\frac{\partial \mathfrak{V}}{\partial n}\,d\omega_1+V_2\int\frac{\partial \mathfrak{V}}{\partial n}\,d\omega_2+V_3\int\frac{\partial \mathfrak{V}}{\partial n}\,d\omega_3+\&c.\\ &=\mathfrak{V}_1\int\frac{\partial V}{\partial n}\,d\omega_1+\mathfrak{V}_2\int\frac{\partial V}{\partial n}\,d\omega_2+\mathfrak{V}_3\int\frac{\partial V}{\partial n}\,d\omega_3+\&c.,\end{aligned}\right\} \quad . \quad (3)$$

in which $d\omega_1$, $d\omega_2$, $d\omega_3$, &c. will be surface-elements of the bodies C_1, C_2, C_3, &c., and the different integrals are to be referred to the surfaces of the respective bodies.

Further, it is known that a simple relation subsists, on the surface of a conducting body charged with electricity, between the differential coefficient, taken in the direction of the normal, of the potential-function, and the electrical density. If, namely, h and $\mathfrak{h}$ denote the surface-densities with the two charges, the equations

$$\frac{\partial V}{\partial n} = -4\pi h \text{ and } \frac{\partial \mathfrak{V}}{\partial n} = -4\pi \mathfrak{h}$$

hold, and thereby (3) is transformed into

$$\left.\begin{aligned} &V_1 \int \mathfrak{h} d\omega_1 + V_2 \int \mathfrak{h} d\omega_2 + V_3 \int \mathfrak{h} d\omega_3 + \&c. \\ &= \mathfrak{V}_1 \int h d\omega_1 + \mathfrak{V}_2 \int h d\omega_2 + \mathfrak{V}_3 \int h d\omega_3 + \&c. \end{aligned}\right\} \quad . \quad . \quad (4)$$

The integrals occurring here again are, however, nothing more than the quantities of electricity present upon the respective bodies; and consequently we obtain the equation which was to be demonstrated:—

$$V_1\mathfrak{Q}_1 + V_2\mathfrak{Q}_2 + V_3\mathfrak{Q}_3 + \&c. = \mathfrak{V}_1 Q_1 + \mathfrak{V}_2 Q_2 + \mathfrak{V}_3 Q_3 + \&c.$$

Now the applications of this equation are facilitated by the fact that it can be still further simplified under certain often occurring conditions.

If, namely, we consider the terms which refer to any one of the given bodies, which may be called C_i, viz. the two products

$$V_i\mathfrak{Q}_i \quad \text{and} \quad \mathfrak{V}_i Q_i,$$

these become in two cases *nil*, so that they can be omitted from the equation. If the body is in conducting connexion with the earth, its potential-level remains at zero with every charge of the system; consequently we have to put for this case

$$V_i = \mathfrak{V}_i = 0,$$

through which the above products vanish. Further, when the body is insulated and initially unelectric, and receives, on charging, no electricity from without, but only through influence undergoes an unequal distribution of its own electricity, then its surface becomes in part positively, and in part negatively electric, in such wise that the total electricity present on the surface remains *nil*. We have consequently then to put

$$Q_i = \mathfrak{Q}_i = 0,$$

through which the above products again vanish. Accordingly

the following rule can be laid down :—Those bodies which during both charges are either in conducting communication with the earth, or insulated and initially unelectric, and in being charged receive no electricity, may be left out of consideration in constructing equation (I.).

It may now, as a special case, be assumed that with all the given bodies, with the exception of C_1 and C_2, one of the two conditions mentioned occurs. The equation then reduces to

$$V_1\mathfrak{Q}_1 + V_2\mathfrak{Q}_2 = \mathfrak{V}_1\mathfrak{Q}_1 + \mathfrak{V}_2 Q_2. \quad . \quad . \quad . \quad . \quad (5)$$

If this equation be still further simplified by making special assumptions respecting the behaviour of the bodies C_1 and C_2, we arrive at the reciprocity-theorems mentioned at the commencement.

We will first suppose the two bodies insulated and initially unelectric, and assume that in the first charging the body C_1 only acquires the quantity of electricity E, by the influence of which the potential-level V_2 is produced in C_2, and that in the second charging only the body C_2 receives the quantity of electricity E, through the influence of which the potential-level $\mathfrak{V}_1$ arises in C_1. In this case we have to put

$$Q_2 = \mathfrak{Q}_1 = 0, \quad Q_1 = \mathfrak{Q}_2 = E,$$

by which (5) is changed into

$$V_2 E = \mathfrak{V}_1 E,$$

or

$$V_2 = \mathfrak{V}_1. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

Consequently the potential-level which arises in C_2 through C_1 being charged with a certain amount of electricity, and that which arises in C_1 through C_2 being charged with the same amount, are equal to one another.

We will make the further assumption, that in the first charging C_1 is charged up to the potential-level K, while C_2 is connected to earth and through influence receives from the earth the amount of electricity Q_2, and that in the second charging C_2 is charged up to the potential-level K, while C_1 is connected to earth and through influence receives the amount $\mathfrak{Q}_1$ of electricity. We have then to put

$$V_2 = \mathfrak{V}_1 = 0, \quad V_1 = \mathfrak{V}_2 = K,$$

whereby (5) is changed into

$$K\mathfrak{Q}_1 = KQ_2,$$

or

$$\mathfrak{Q}_1 = Q_2. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

Consequently the amount of electricity which through influ-

ence is collected on C_2 when C_1 is charged up to a certain potential-level, and that which in the charging of C_2 up to the same potential is through influence collected on C_1, are equal the one to the other.

Beside these two conclusions, here cited as examples, referable to two very simple special cases, from equation (I.) many other similar inferences can of course be drawn.

LX. *On the Potential of an Ellipsoid at an External Point.* *By* Colonel A. R. Clarke, *C.B., F.R.S.**

IN connexion with the subject of the attraction of the earth upon external objects, there is a series which is usually brought forward by writers on astronomy, viz. that which results from expanding into a series in descending powers of r the expression for V,

$$V=\iiint \frac{dx\,dy\,dz}{\{(f-x)^2+(g-y)^2+(h-z)^2\}^{\frac{1}{2}}},$$

r being the distance $=(f^2+g^2+h^2)^{\frac{1}{2}}$ of the attracted external particle from the origin, x, y, z the coordinates of any element of the mass, the density being unity throughout. Put $x^2+y^2+z^2=\rho^2$, $\alpha x+\beta y+\gamma z=\sigma$, where α, β, γ are the direction-cosines of r; then the radical in the expression for V may be expanded in the form

$$\frac{1}{r}+\frac{Q_1}{r^2}+\frac{Q_2}{r^3}+\frac{Q_3}{r^4}+\ldots,$$

where Q_i is a homogeneous function of x, y, z of the degree i. When the body is an ellipsoid referred to its principal axes, the terms in which i is odd will disappear in integrating over the volume of the ellipsoid; so that in this case, M being the mass of the ellipsoid,

$$V=\frac{M}{r}+\frac{1}{r^3}\int Q_2 dm+\frac{1}{r^5}\int Q_4 dm+\frac{1}{r^7}\int Q_6 dm+\ldots, \quad (1)$$

which is the series alluded to. Lagrange's investigation of the terms (as far as just written down) of this series is referred to in Todhunter's 'History of the Theory of Attraction and the Figure of the Earth,' vol. ii. p. 161. See also Thomson and Tait, 'Natural Philosophy,' pp. 401, 402; Pontécoulant, *Théorie Analytique du Système du Monde*, ii. p. 233, where the above expression for the potential is given as one suitable

* Communicated by the Author.

only when r, as compared with the dimensions of the attracting body, is very large—as, for instance, in the investigation of the disturbance of the moon's motion produced by the non-sphericity of the earth, and of the reaction of the same disturbing force on the earth, causing lunar nutation and precession. But the fact is, that the first two terms of the series are sufficient for any external point, however near, provided the square of the earth's ellipticity be neglected; for the ratio of the successive terms is not of the order $\frac{a^2}{r^2}$, but $\frac{a^2-b^2}{r^2}$, a, b being the semidiameters of the earth.

If P_n be Legendre's coefficient of the order n, then we have, μ being the cosine of the angle between r and ρ,

$$(r^2-2r\rho\mu+\rho^2)^{-\frac{1}{2}}=\frac{P_0}{r}+\frac{P_1\rho}{r^2}+\frac{P_2\rho^2}{r^3}+\frac{P_3\rho^3}{r^4}+\ldots;$$

consequently

$$\int Q_i dm=\int P_i\rho^i dm.$$

Now we require only the even coefficients; and their values (Todhunter's 'Functions of Laplace, Lamé, and Bessel,' p. 4) are:—

$$P_2=\frac{3}{2}\mu^2-\frac{1}{2},$$

$$P_4=\frac{5.7}{2.4}\mu^4-\frac{3.5}{2.4}2\mu^2+\frac{1.3}{2.4},$$

$$P_6=\frac{7.9.11}{2.4.6}\mu^6-\frac{5.7.9}{2.4.6}3\mu^4+\frac{3.5.7}{2.4.6}3\mu^2-\frac{1.3.5}{2.4.6};$$

whence the values of Q, since $\rho\mu=\sigma$, are

$$Q_2=\frac{3}{2}\sigma^2-\frac{1}{2}\rho^2,$$

$$Q_4=\frac{5.7}{2.4}\sigma^4-\frac{3.5}{2.4}2\sigma^2\rho^2+\frac{1.3}{2.4}\rho^4,$$

$$Q_6=\frac{7.9.11}{2.4.6}\sigma^6-\frac{5.7.9}{2.4.6}3\sigma^4\rho^2+\frac{3.5.7}{2.4.6}3\sigma^2\rho^4-\frac{1.3.5}{2.4.6}\rho^6.$$

For the integration of Q_2 we have

$$\int x^2dm=\frac{M}{5}a^2:\int y^2dm=\frac{M}{5}b^2:\int z^2dm=\frac{M}{5}c^2;$$

and there is no difficulty in arriving at the equation

$$\int Q_2 dm=-\frac{M}{15}\{P_2'(e_2^2-e_3^2)+P_2''(e_3^2-e_1^2)+P_2'''(e_1^2-e_2^2)\}, \quad (2)$$

where $e_1^2=b^2-c^2$; $e_2^2=c^2-a^2$; $e_3^2=a^2-b^2$; and P_2', P_2'', P_2''' are what P_2 becomes when α, β, γ are respectively written for μ.

We may write the next term thus,

$$Q_4=Ax^4+By^4+Cz^4+A'x^2y^2+B'y^2z^2+C'z^2x^2+W,$$

where W includes all terms in which the exponents are odd, which disappear in integration. But Q_i must satisfy the differential equation

$$\frac{d^2Q_i}{dx^2}+\frac{d^2Q_i}{dy^2}+\frac{d^2Q_i}{dz^2}=0. \quad . \quad . \quad . \quad . \quad (3)$$

Applying this to Q_4, and remembering that the equation is identically true, we get these equations:—

$$6A+A'+C'=0,$$
$$6B+A'+B'=0,$$
$$6C+B'+C'=0,$$

whence

$$A'+3(\ \ A+B-C)=0,$$
$$B'+3(-A+B+C)=0,$$
$$C'+3(\ \ A-B+C)=0.$$

On integrating the expression for Q_4, after substituting these values of A′, B′, C′, it is to be observed that

$$\int x^4dm=\frac{1.3}{5.7}Ma^4; \quad \int x^2y^2dm=\frac{1}{5.7}Ma^2b^2,$$

with corresponding values for the other integrals. Also A, B, C are equal respectively to P_4', P_4'', P_4''', where the accents have the meaning already explained. Thus we get

$$\int Q_4dm=-\frac{3M}{5.7}\{P_4'e_3^2e_2^2+P_4''e_1^2e_3^2+P_4'''e_2^2e_1^2\}. \quad . \quad (4)$$

For the next term put $Q_6=I_1\sigma^6+I_2\sigma^4\rho^2+I_3\sigma^2\rho^4+I_4\rho^6$; and then, expanding, we get

$$Q_6=Ax^6+By^6+Cz^6+A_1x^2y^4+A_2x^4y^2+B_1y^2z^4+B_2y^4z^2$$
$$+C_1z^2x^4+C_2z^4x^2+Ex^2y^2z^2$$

plus terms involving odd powers of x, y, z, which disappear in integration. On substituting Q_6 in the differential equation (3), which it has to satisfy, the following relations are found amongst the coefficients with which we are concerned :—

$$15A+A_2+C_1=0, \qquad 6A_1+6A_2+E=0,$$
$$15B+A_1+B_2=0, \qquad 6B_1+6B_2+E=0,$$
$$15C+C_2+B_1=0, \qquad 6C_1+6C_2+E=0.$$

We cannot from these six equations express A_1, A_2, B_1, B_2, C_1, C_2 in terms of the other four coefficients, because on comparing the sums of the two sets of equations we get $E=30(A+B+C)$; therefore we must seek some simple relation amongst the coefficients that may be used as another equation. The coefficients are

$$A = I_1\alpha^6 + I_2\alpha^4 + I_3\alpha^2 + I_4,$$

$$A_1 = 15I_1\alpha^2\beta^4 + I_2(6\alpha^2\beta^2 + \beta^4) + I_3(\alpha^2 + 2\beta^2) + 3I_4,$$

$$A_2 = 15I_1\alpha^4\beta^2 + I_2(6\alpha^2\beta^2 + \alpha^4) + I_3(2\alpha^2 + \beta^2) + 3I_4,$$

from which the others may be written down. The simplest relation that suggests itself arises from adding the three differences $A_1-A_2+B_1-B_2+C_1-C_2$; this is equal to

$$15I_1(\beta^2-\gamma^2)(\gamma^2-\alpha^2)(\alpha^2-\beta^2) = 15P. \quad . \quad . \quad (5)$$

Also $A=P_6' : B=P_6'' : C=P_6'''$, the accents having the meaning already explained. Thus we get

$$\begin{aligned}
\tfrac{2}{5}A_1 &= \ P_0 + \ P_6' - 3P_6'' - \ P_6''',\\
\tfrac{2}{5}A_2 &= -P_0 - 3P_6' + \ P_6'' - \ P_6''',\\
\tfrac{2}{5}B_1 &= \ P_0 - \ P_6' + \ P_6'' - 3P_6''',\\
\tfrac{2}{5}B_2 &= -P_0 - \ P_6' - 3P_6'' + \ P_6''',\\
\tfrac{2}{5}C_1 &= \ P_0 - 3P_6' - \ P_6'' + \ P_6''',\\
\tfrac{2}{5}C_2 &= -P_0 + \ P_6' - \ P_6'' - 3P_6'''.
\end{aligned}$$

These have to be substituted in Q_6, with the following values for the integrals:—

$$\int x^6 dm = \frac{1.3.5}{5.7.9} Ma^6 : \int x^2y^4 dm = \frac{1.3}{5.7.9} Ma^2b^4 :$$

$$\int x^2y^2z^2 dm = \frac{M}{5.7.9} a^2b^2c^2.$$

The result is

$$\begin{aligned}
\int Q_6 dm = \frac{1.3}{7.9}\frac{M}{2}\{&P_6' e_2^2e_3^2(e_2^2-e_3^2) + P_6'' e_3^2e_1^2(e_3^2-e_1^2)\\
&+ P_6''' e_1^2e_2^2(e_1^2-e_2^2) + Pe_1^2e_2^2e_3^2\}. \quad (6)
\end{aligned}$$

The sequence of the terms (2), (4), (6), which complete the series (1) as far as written down, is very remarkable, and suggests the idea that possibly an expression might be obtained for the general term. When the ellipsoid is one of revolution, so that $c=b$, and $e^2=c^2-a^2$,

$$V = \frac{M}{r}\left\{1 - \frac{3P_2'}{3.5}\cdot\frac{e^2}{r^2} + \frac{3P_4'}{5.7}\cdot\frac{e^4}{r^4} - \frac{3P_6'}{7.9}\cdot\frac{e^6}{r^6} + \dots\right\}.$$

LXI. *A Modification of* Dumas's *Method of Determining Vapour-Densities. By* J. Habermann *.

As the significance of the knowledge of the vapour-densities of substances in relation to the doctrine of modern chemistry is gradually being more fully recognized, chemists are striving to simplify the methods of Gay-Lussac and Dumas (the two chief processes at present in use for obtaining such knowledge), and at the same time to render them more accurate and of wider applicability.

In the year 1862, H. Schiff, in describing a modification of Gay-Lussac's method, says, "In spite of all the improvements which have hitherto been proposed, chemists seem to prefer to adopt the method of Dumas in making determinations at low temperatures." At the present time, however, the opposite appears to be the case.

Since the time of Hofmann's improvement of Gay-Lussac's method, the efforts of chemists towards perfecting the modes of determining vapour-densities have principally been directed to removing the disadvantages connected with the Hofmann-Gay-Lussac method, and to making it applicable to bodies which boil at a high temperature. As a result of these investigations, we have existing at the present time no less than three memoirs relating to the subject.

The last publications treating of improvements of Dumas's method were made some years ago by Deville and Troost, and Bunsen. The object of the two first-named investigators was to extend the limit of temperature to which the method is applicable beyond the boiling-point of zinc. Bunsen so varied the process that by his modification it is possible to obtain the vapour-densities of bodies by a determination depending merely on two weight-differences; and this can be done with a degree of accuracy hitherto hardly known. The care and attention needed in carrying out this method, however, are increased in a ratio corresponding to this accuracy; and in consequence the modified process up to the present time has not been very generally adopted, more especially as it fails to remove certain important disadvantages of the original method. Later suggestions for improvement in this direction are entirely wanting; and in consequence, whenever practicable, the method of Dumas is dispensed with, since, to quote Victor Meyer, "it necessitates a loss in material of about three grams, and is therefore not easily applicable to the greater number of newly discovered bodies." Moreover, since it requires a temperature greatly exceeding the boiling-point of the substance, the determination

* Freely translated from Liebig's *Annalen*, June 9, 1877, by John I. Watts.

of the vapour-density becomes impossible in the case of a number of bodies.

It must appear rather surprising that no attempt has been made to extend to Dumas's method the same artifice which Hofmann has so successfully applied to that of Gay-Lussac—namely, to make the determination of the density of the vapour under diminished pressure. I have made such an attempt, and believe that I have succeeded by very simple arrangements in proving that it is possible :—

(1) to make a determination of a vapour-density by Dumas's method with less than a gram of the substance ;

(2) to recover without difficulty the greater part of the substance employed, free from impurity ;

(3) to effect the determination at a temperature which need never exceed the boiling-point of the substance.

In the execution of the experiments about to be described, which were made with bodies whose boiling-points extended up to 250°, there were needed, in addition to the glass balloon, a moderately large thick-walled bulb-tube, an aspirator with a mercury manometer, a thermometer, a barometer, and an oil-bath—things, therefore, which are hardly wanting in any laboratory.

It is scarcely necessary to say any thing with respect to the glass balloon ; for if suitable for Dumas's method, it is equally applicable to the modified process. It may conveniently have a capacity of from 250 cubic centims. to 300 cubic centims., although (as the examples show) it may be considerably less. The neck of the balloon, which should previously be carefully cleaned and dried, is drawn out to a capillary tube 2 millims. in diameter, of suitable length, and as thick as possible in its wall. The capillary tube is twice bent, in a manner which will be perfectly evident from the figure (p. 465). The position of the two bendings is dependent upon the size of the balloon and the diameter of the vessel used for the oil-bath ; matters should, however, be so arranged that when the balloon is sunk in the bath the second bending just appears above the opening of the vessel and near its edge. At this bend the capillary tube constituting the neck is to be further constricted to a diameter of 1 millim ; the open end of course can be closed before the blowpipe. The bulb-tube employed as the receiver is also bent to an obtuse angle. The portion of the tube containing the bulbs is so drawn out at the end, that the thick caoutchouc tube of the pump can be conveniently pushed over it ; whilst the end of the shorter arm is adapted, by a short length of sufficiently stout caoutchouc tube, to the balloon.

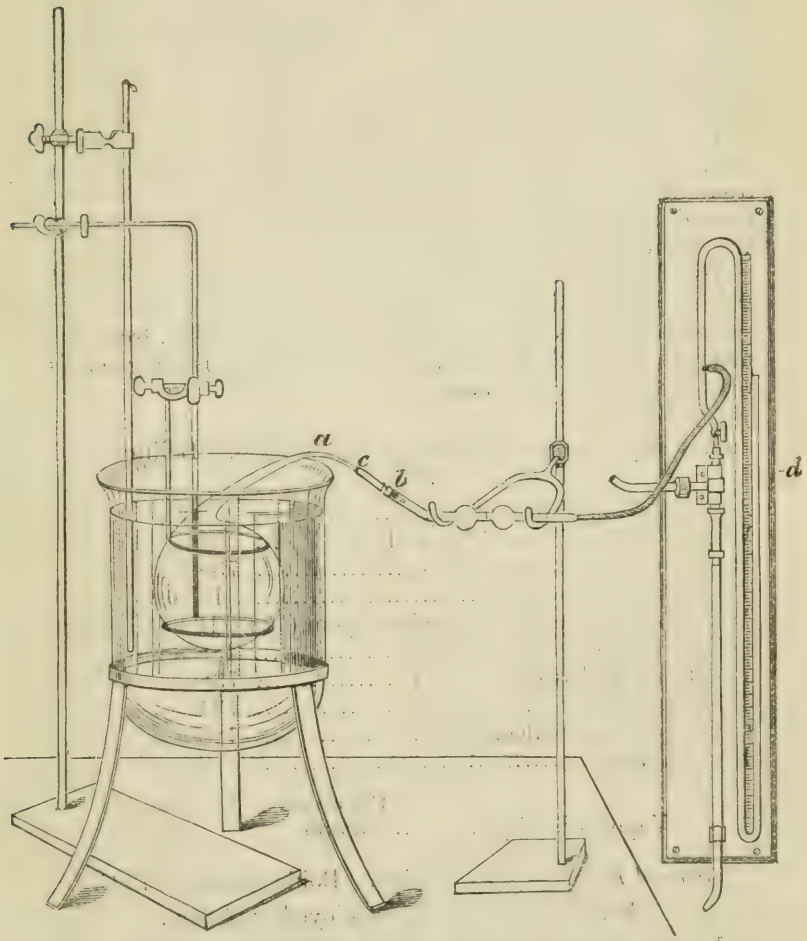
The experiments are carried out in precisely the mode described by Dumas ; that is, the balloon filled with air is weighed, the barometer and thermometer are noted, and all the other well-known precautions which influence the accuracy of the results are taken. About a gram of the substance is introduced into the balloon in the ordinary way ; it is then clamped between two iron rings in the position indicated in the figure, and sunk to a suitable depth in the bath. The bending, *a*, of the capillary neck must be in proximity to the edge of the vessel and yet above it. The open end of the capillary tube projects beyond the edge of the vessel without touching it, and is inclined upwards. One end of the bulb-tube is connected with the pump, and the other end with the capillary neck of the balloon by means of the caoutchouc tube, in such a manner that about 1 centim. of the caoutchouc tube is within the bulb-tube. The position which the bulb-tube assumes will be evident from the figure. It may be supported on a movable stand.

If the caoutchouc connexion at *b* is suitably adjusted, which is very easily effected, and the connexion with the pump made with care, the apparatus will be air-tight, and the experiment may be commenced. The small balloons are evacuated up to a pressure of 500 millims., the larger to 600 millims. and upwards, as indicated on the manometer; the cock *d* is then closed and heat is applied.

The liquid in the balloon is rapidly heated until it commences to boil, which is readily known from the passing of drops over into the receiver; and the flame is so regulated that the temperature of the bath rises about 1° in from 1 to 2 minutes. When the thermometer in the oil-bath indicates a temperature about 10° or 20° below the boiling-point of the substance employed, the evacuation is reinstituted until the mercury column in the manometer, which meanwhile will have fallen a few centimetres in consequence of the higher temperature and the vapour-tension, has risen to its original height, the portion of the capillary tube projecting out of the bath up to the bend *a* being bathed uninterruptedly in the liquid of the bath.

When the thermometer in the oil-bath nearly indicates the boiling-point of the substance, the neck at *c* is softened by means of the blowpipe-flame and the balloon is sealed by drawing away the bulb-tube, which under the given circumstances can be done with great ease and without risk to the experiment. Of course, the temperature of the oil-bath and the heights of the manometer and barometer are at the same time noted. I have never perceived in my experiments that, at the temperature of sealing, liquid still distilled over out of

the balloon. The facility with which the balloon can be sealed up is not among the least of the advantages of my modification. On softening the glass at *c* by means of the blowpipe-flame, the capillary tube immediately collapses by the pressure of the air; and the fine glass threads formed by the withdrawal of the bulb-tube can easily be melted before the flame into a bead. The reading-off of the manometer needs



no particular hurry, because its height is comparatively fixed by the withdrawal of the bulb-tube.

The height of the manometer having been read off, the air

is admitted into the receiver, and the rest of the process carried out as directed by Dumas.

With substances of comparatively high melting-points and which on cooling rapidly solidify, like benzoic acid, it is advisable to make a slight alteration.

The neck of the carefully cleaned balloon is not to be drawn out into a capillary tube, but simply narrowed to the dimensions above given, and connected directly with the aspirator. There is then no danger of the solidifying distillate stopping up the neck of the tube, as the solidification can only take place in that part of the neck of the balloon which is situated outside the oil-bath, where the substance can easily be again liquefied by means of a spirit-lamp.

Scarcely any remark is necessary respecting the calculation. Suffice it to say that, in the reduction of the volume from the temperature at which the sealing is made, I take, instead of the barometric pressure, the difference between that and the reading of the manometer.

The degree of applicability of the method here described may be judged of by the following examples; I will merely premise that the time needed for the estimation, from the moment in which the balloon filled with air is weighed, is scarcely more than an hour.

First Experiment.—Anhydrous Acetic Acid. Boiling-point 137°.

Amount of substance employed	0·6 grm.
Weight of the balloon filled with air (P)	18·9572 grms.
Height of the barometer (B)	738·5 millims.
Temperature (t)	16°·6 C.
Weight of the balloon filled with vapour (P_1)	18·9340 grms.
Height of the manometer (M)	488 millims.
Height of the barometer (B_1)	738·5 millims.
Temperature (t_1)	134° C.
Capacity of the balloon (V)	120·5 cub. cent.
Residual air	0·5 cub. cent.

	Calculated.	Found.
Vapour-density	3·536	3·528

Second Experiment.—Aniline. Boiling-point 181° C.

Amount of substance employed 0·92 grm.

P = 45·7606 grms., B = 744·5 millims., t = 16°·2 C.
P_1 = 45·5770 grms., B_1 = 744·5 millims., t_1 = 168° C.

M = 553 millims., V = 353·8 cubic centims.

	Calculated.	Found.
Vapour-density	3·224	3·360

Third Experiment.—Benzoic Acid. Melting-point 120° C. Purified by repeated sublimation.

Amount of substance employed 0·83 grm.

P = 39·1488 grms., B = 745 millims., t = 17° C.
P_1 = 38·9430 grms., B_1 = 745·5 millims., t_1 = 229° C.

M = 605 millims., V = 330·8 cub. cent.

	Calculated.	Found.
Vapour-density	4·2042	4·398

Fourth Experiment.—Dimethylhydroquinon. Boiling-point 204° to 205° C.

Amount of substance employed 0·73 grm.

P = 44·3440 grms., B = 745 millims., t = 17°·5 C.
P_1 = 44·1935 grms., B_1 = 744 millims., t_1 = 201° C.

M = 575 millims., V = 352 cub. cent.
Residual air..... = 1·5 „ „

	Calculated.	Found.
Vapour-density	4·772	4·741

Fifth Experiment.—Dimethylresorcin. Boiling-point 214° to 215° C.

Amount of substance employed 0·5 grm.

P = 34·3014 grms., B = 744 millims., t = 17° C.
P_1 = 34·131 grms., B_1 = 744 millims., t_1 = 211° C.

M = 605 millims., V = 266 cub. cent.,
Residual air..... = 3·6 „

	Calculated.	Found.
Vapour-density	4·772	4·69

Sixth Experiment.—Dimethylresorcin.

P = 37·102 grms., B = 744 millims., t = 17°·6 C.
P_1 = 36·8744 grms., B_1 = 744 millims., t_1 = 211°·5 C.

M = 670 millims., V = 265·6 cub. cent.

	Found.
Vapour-density.....	4·705

The product, as proved by analysis, still contained some monomethylresorcin.

The preceding data are sufficient, to my thinking, to prove the usefulness of the modified Dumas's method of vapour-density determinations ; my efforts will now be further directed to making this modification applicable to cases where both the oil-bath and the mercury thermometer are inapplicable.

LXII. *Intelligence and Miscellaneous Articles.*

ON THE MAGNETIZATION OF STEEL TUBES. BY J.-M. GAUGAIN.

IF into a magnetized steel tube, at the ordinary temperature, a cylindrical core of the same metal in the neutral state be introduced, and again taken out after the lapse of a few moments, it will be found to be magnetized in the same direction as the tube. But if, after placing the core in the tube, we heat the system with a lamp so as to raise its temperature to about 300°, let it cool again, and after cooling separate the tube from the core, we find that the tube has lost a great part of its previous magnetism, and that the core has acquired a contrary magnetization.

I suppose that even at the ordinary temperature the core takes a magnetization the inverse of that of the tube as long as it remains within the latter ; but when we come to take it out, friction is inevitably produced, the result of which is the reversal of the direction of the magnetization. If things happen otherwise when we operate at an elevated temperature, it is because, on the one hand, the inverse magnetization developed in the core by the influence of the tube is considerably augmented by the heating, and, on the other, the direct magnetization developed at the moment of separation of the tube and the core is weakened, the tube having lost the greater part of its magnetism when the separation takes place. In consequence of both these circumstances the inverse magnetization remains predominant.

Altogether analogous effects to those just indicated are produced when a magnetized core of steel is introduced into a tube of the same metal in the neutral state : if the operation takes place at the ordinary temperature, the tube is found, when separated from the core, to be magnetized in the same direction as the latter ; but if the system be heated and the tube be not separated from the core until after cooling, the tube will have acquired the inverse magnetization.

For the heating of the system to develop this inverse magnetism in one of its parts (tube or core), it is not indispensable that this part shall be in the neutral state. When the two parts are magnetized in the same direction, but unequally, and there is sufficient difference between their magnetizations, the feebler of these is reversed when the system is heated.

Let us now consider the case in which the system formed of a tube and a core of steel in the neutral state is magnetized by Elias's process. If the magnetization is effected at the ordinary temperature, we find that the tube and core, separated from one another, are magnetized in the same direction; this was verified by M. Jamin (*Comptes Rendus*, Feb. 15, 1875). The same result is again obtained when the system is magnetized at a high temperature (300–400°), and the tube and core separated immediately after the magnetization is effected; but when, after having magnetized the system while hot, we leave the tube and core to cool in contact with one another, we find, on separating them when quite cold, that they are generally magnetized in directions the one the inverse of the other; it is only in a particular case that they are both magnetized in the same direction. The sign of the magnetization varies with the thickness of the tube, the coercive force of the steel, and the intensity of the current used for developing the magnetization.

I have performed a first series of experiments, on tubes whose thicknesses were $\frac{1}{4}$, $\frac{1}{2}$, $\frac{3}{4}$, and 1 millim.; each of these tubes was 10 millims. in exterior diameter, and about 300 millims. in length. They had been *drawn* and manufactured, as well as the cores with which they were supplied, of steel known in commerce under the name of "soft Petin-Godet."

The following Table contains the results obtained in operating upon the tube half a millimetre in thickness.

I.	M.	M′.	*m*.	*m*′.
3·4	+ 4·6	+ 8·0	− 1·5	+ 5·0
7·5	+20·0	+22·2	+ 2·5	+ 2·5
14·5	+56·0	+21·0	+17·2	−15·0
20·0	+80·0	+27·0	+28·2	−25·1
29·0	+80·0	+30·2	+28·0	−28·0
38·0	+87·0	+34·0	+24·0	−29·5

The numbers in the column marked I represent the intensities of the current made use of to effect the magnetization. The letters M and M′ designate respectively the values of the magnetisms of the core and the tube when these are measured immediately after the magnetization effected before the cooling; while *m* and *m*′ denote the values of the magnetisms of the core and tube respectively, measured after the cooling of the system. I regard as positive the direct magnetization, and as negative the inverse. I call *direct* magnetization that which would be communicated by the current at the ordinary temperature, whether to the tube or to the core.

On inspecting the Table we see that the magnetism *m* of the core, at first inverse for the very feeble current I=3·4, becomes direct when the intensity of the current augments, and that, on the contrary, the magnetism *m*′ of the tube, direct with the currents 3·4 and 7·5, becomes inverse for currents of greater intensity.

These results may be regarded as consequences of a more simple fact, which I have noticed at the commencement of this

Note. In fact, from the preceding Table it follows that the core and the tube are magnetized in the same direction before the cooling of the system, that the initial magnetization M′ of the tube surpasses that of the core while the current is feeble, but that the magnetization M of the core excels that of the tube when the intensity of the current passes a certain limit. Accordingly it is the magnetism of the core that will be reversed during the cooling, in the case of feeble currents, and, on the contrary, the magnetism of the tube that has to undergo reversal in the case of more energetic currents.

In regard to the different quantitative ratios which establish themselves between the two magnetisms M and M′, according as the current is more or less intense, they are easily accounted for by starting from the principle laid down by M. Jamin, that the current penetrates to a greater depth the more energetic it is.

The experiments performed upon the tubes of $\frac{1}{4}$, $\frac{3}{4}$, and 1 millim. thickness gave results entirely analogous to those which I have here described.—*Comptes Rendus de l'Académie des Sciences*, Oct. 1, 1877, tome lxxxv. pp. 615–617.

ON THE DISAGGREGATION OF TIN.

The observation has been made before, that organ-pipes after long use become brittle and fall to pieces. In a similar manner, as stated by Oudemans *, plates of pure tin, containing at the most only 0·3 per cent. of lead and iron, have, during conveyance by railway from Rotterdam to Moscow in severe cold, broken into small fragments resembling sulphide of molybdenum.

According to a trustworthy communication from the Royal Pyrotechnic Laboratory at Spandau, a similar phenomenon has been recently observed. A large quantity (295 kilograms) of tin-plate acquired laminar exfoliations, in which it crumbled into minute particles. Similarly, but in a less degree, larger quantities (1950 kilograms) of blocks of tin subsequently suffered. The warehouses were thoroughly dry; the tin contained merely traces of foreign metals, no sulphur or phosphorus, and no oxide of tin. According to the account of Dr. Petri, the tin could be more easily pulverized than filings of unaltered tin, and evolved hydrogen more quickly with acid. Within the time during which it lay in the warehouse there was no severe winter; and, moreover, the disaggregation continued.

From all these observations it appears probable that in this disaggregation the repeated little shocks, combined with frequent strong variations of temperature (for example, considerable refrigerations), essentially cooperated.—Poggendorff's *Annalen*, 1877, No. 10; new series, vol. ii. p. 304.

* *Chem. Jahresb.* 1872, p. 256.

ON THE EXACT MEASURE OF THE HEAT OF SOLUTION OF SULPHURIC ACID IN WATER. BY M. CROULLEBOIS.

The heat produced by the mixture of monohydrated sulphuric acid with variable quantities of water has been already measured by divers physicists; but their results present rather great divergences. M. Pfaundler has recently resumed the investigation of this question, and has represented by a simple formula the quantity Q_n of heat evolved by 1 molecule of SO_4H_2 when n molecules of water are added. The formula is

$$Q_n = \frac{nB}{n+A}.$$

But the work accomplished by M. Pfaundler, notwithstanding the progress realized, is still incomplete; for the preceding formula does not include the temperature at which the determinations were effected. Now M. Kirchhoff has shown, long since, that the thermic effect is intimately connected with the tension of the vapour of water emitted by the solution, and consequently with the temperature. Doubtless it is here that we must seek the explanation of the divergent results. In view of these facts I shall compare the numbers furnished by M. Pfaundler's formula with those which may be deduced from the relation given by M. Kirchhoff. This relation can be obtained in several ways, and more quickly than it was by the illustrious physicist in his memoir on the internal energy of bodies. Here we shall proceed as follows:—

Consider two states, A and B, of the operative substance. In the state A an indefinitely small quantity dx of water is *in presence* of the acid, at the absolute temperature t; in the state B the same quantity is *in solution* in the acid, at the same temperature. It is possible to pass from one state to the other by two different paths: either the solution is effected directly, and the variation of internal energy, *approximately* equal to the heat evolved, is dQ; or else the two extreme states can be joined by moving a *characteristic* point upon three *isothermal* lines.

1. The solution emits the quantity dx of vapour, at tension f; the variation of internal energy is $du = (l - Af\sigma)dx$.

2. This vapour, separated from the dissolvant, is compressed at the temperature t so that f becomes equal to F; the variation of energy is *nil*.

3. After the limit of saturation is attained, the compression is continued till the weight dx of vapour is brought back to the liquid state; the variation of energy is $du' = (L - AF\Sigma)dx$.

l, L, f, F, A have the usual significations; σ and Σ designate respectively the difference between the volume of the vapour and that of the liquid under the corresponding tensions f and F.

It is known that the variation of internal energy depends only on the initial and the final state; we have therefore

$$dQ = du' - du = L\left(1 - \frac{l}{L}\right)dx,$$

with permissible approximation. To render this expression calculable I substitute for l and L their values according to Clapeyron's formula, and obtain

$$dQ=L\left(1-\frac{At\sigma\frac{df}{dt}}{At\Sigma\frac{dF}{dt}}\right)dx=L\left(1-\frac{\frac{df}{dt}}{\frac{dF}{dt}}\frac{F}{f}\right)dx.$$

The addition of a weight $x-x_0$ of water will evolve a quantity of heat given by the integral

$$Q=L\int_{x_0}^{x}\left(1-\frac{\frac{df}{dt}}{\frac{dF}{dt}}\frac{F}{f}\right)dx.$$

f, F, L are given by the experiments of M. Regnault; and from them we deduce $\frac{df}{dt}$ and $\frac{dF}{dt}$. Besides, if $x-x_0$ is slight, we readily perceive that the mean value of the element (which varies with $x-x_0$) of the integral is obviously the mean of the values taken by the ratio $\frac{\frac{df}{dt}}{f}$ after the addition of the weights x_0 and x of water.

This being admitted, what is the quantity of heat evolved, for example, when H_2O is mixed with $SO_4H_2+H_2O$? M. Pfaundler's formula gives 3048 calories. M. Kirchhoff's relation gives the following figures:—

Temperatures.	Calories.
10	4554
20	3168
21	2887
22	2648
24	2420

M. Pfaundler's measure was probably taken in the vicinity of 20°.

The above Table shows the influence of temperature in calometric determinations of this order, and sets forth what is wanting for a complete investigation of the question. However, M. Kirchhoff's relation, presented under the foregoing form, and consequently rendered quickly calculable, may be considered sufficient until direct measurements are obtained.—*Comptes Rendus de l'Académie des Sciences*, Oct. 1, 1877, tome lxxxv. pp. 617–619.

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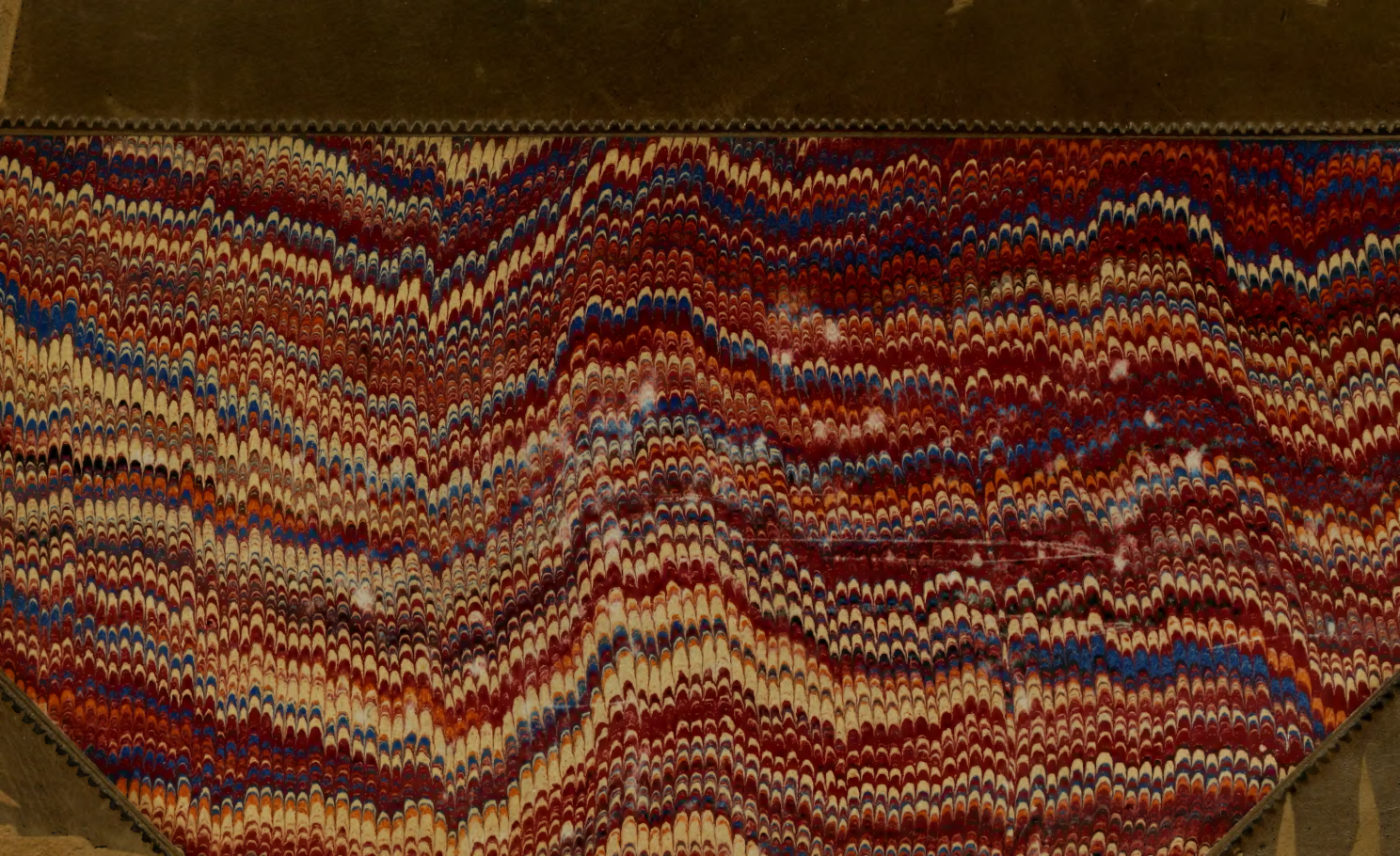
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